

Encyclopedia of
Complexity and Systems Science Series
Editor-in-Chief: Robert A. Meyers

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Bulbul Chakraborty
Editor

Statistical and Nonlinear Physics

A Volume in the Encyclopedia of
Complexity and Systems Science,
Second Edition

Encyclopedia of Complexity and Systems Science Series

Editor-in-Chief

Robert A. Meyers

The Encyclopedia of Complexity and Systems Science series of topical volumes provides an authoritative source for understanding and applying the concepts of complexity theory, together with the tools and measures for analyzing complex systems in all fields of science and engineering. Many phenomena at all scales in science and engineering have the characteristics of complex systems, and can be fully understood only through the transdisciplinary perspectives, theories, and tools of self-organization, synergetics, dynamical systems, turbulence, catastrophes, instabilities, nonlinearity, stochastic processes, chaos, neural networks, cellular automata, adaptive systems, genetic algorithms, and so on. Examples of near-term problems and major unknowns that can be approached through complexity and systems science include: The structure, history and future of the universe; the biological basis of consciousness; the integration of genomics, proteomics and bioinformatics as systems biology; human longevity limits; the limits of computing; sustainability of human societies and life on earth; predictability, dynamics and extent of earthquakes, hurricanes, tsunamis, and other natural disasters; the dynamics of turbulent flows; lasers or fluids in physics, microprocessor design; macromolecular assembly in chemistry and biophysics; brain functions in cognitive neuroscience; climate change; ecosystem management; traffic management; and business cycles. All these seemingly diverse kinds of phenomena and structure formation have a number of important features and underlying structures in common. These deep structural similarities can be exploited to transfer analytical methods and understanding from one field to another. This unique work will extend the influence of complexity and system science to a much wider audience than has been possible to date.

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Bulbul Chakraborty
Editor

Statistical and Nonlinear Physics

A Volume in the Encyclopedia of Complexity
and Systems Science, Second Edition

With 300 Figures and 10 Tables

 Springer

Editor

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Series Preface

The Encyclopedia of Complexity and System Science Series is a multivolume authoritative source for understanding and applying the basic tenets of complexity and systems theory as well as the tools and measures for analyzing complex systems in science, engineering, and many areas of social, financial, and business interactions. It is written for an audience of advanced university undergraduate and graduate students, professors, and professionals in a wide range of fields who must manage complexity on scales ranging from the atomic and molecular to the societal and global.

Complex systems are systems that comprise many interacting parts with the ability to generate a new quality of collective behavior through selforganization, e.g., the spontaneous formation of temporal, spatial, or functional structures. They are therefore adaptive as they evolve and may contain self-driving feedback loops. Thus, complex systems are much more than a sum of their parts. Complex systems are often characterized as having extreme sensitivity to initial conditions as well as emergent behavior that are not readily predictable or even completely deterministic. The conclusion is that a reductionist (bottom-up) approach is often an incomplete description of a phenomenon.

This recognition that the collective behavior of the whole system cannot be simply inferred from the understanding of the behavior of the individual components has led to many new concepts and sophisticated mathematical and modeling tools for application to many scientific, engineering, and societal issues that can be adequately described only in terms of complexity and complex systems.

Examples of Grand Scientific Challenges which can be approached through complexity and systems science include: the structure, history, and future of the universe; the biological basis of consciousness; the true complexity of the genetic makeup and molecular functioning of humans (genetics and epigenetics) and other life forms; human longevity limits; unification of the laws of physics; the dynamics and extent of climate change and the effects of climate change; extending the boundaries of and understanding the theoretical limits of computing; sustainability of life on the earth; workings of the interior of the earth; predictability, dynamics, and extent of earthquakes, tsunamis, and other natural disasters; dynamics of turbulent flows and the motion of granular materials; the structure of atoms as expressed in the Standard Model and the formulation of the Standard Model and gravity into a Unified Theory; the structure of water; control of global infectious diseases; and also evolution and quantification of

(ultimately) human cooperative behavior in politics, economics, business systems, and social interactions. In fact, most of these issues have identified nonlinearities and are beginning to be addressed with nonlinear techniques, e.g., human longevity limits, the Standard Model, climate change, earthquake prediction, workings of the earth's interior, natural disaster prediction, etc.

The individual complex systems mathematical and modeling tools and scientific and engineering applications that comprised the *Encyclopedia of Complexity and Systems Science* are being completely updated and the majority will be published as individual books edited by experts in each field who are eminent university faculty members.

The topics are as follows:

Agent Based Modeling and Simulation
 Applications of Physics and Mathematics to Social Science
 Cellular Automata, Mathematical Basis of
 Chaos and Complexity in Astrophysics
 Climate Modeling, Global Warming, and Weather Prediction
 Complex Networks and Graph Theory
 Complexity and Nonlinearity in Autonomous Robotics
 Complexity in Computational Chemistry
 Complexity in Earthquakes, Tsunamis, and Volcanoes, and Forecasting and
 Early Warning of Their Hazards
 Computational and Theoretical Nanoscience
 Control and Dynamical Systems
 Data Mining and Knowledge Discovery
 Ecological Complexity
 Ergodic Theory
 Finance and Econometrics
 Fractals and Multifractals
 Game Theory
 Granular Computing
 Intelligent Systems
 Nonlinear Ordinary Differential Equations and Dynamical Systems
 Nonlinear Partial Differential Equations
 Percolation
 Perturbation Theory
 Probability and Statistics in Complex Systems
 Quantum Information Science
 Social Network Analysis
 Soft Computing
 Solitons
 Statistical and Nonlinear Physics
 Synergetics
 System Dynamics
 Systems Biology

Each entry in each of the Series books was selected and peer reviews organized by one of our university-based book Editors with advice and consultation provided by our eminent Board Members and the Editor-in-Chief.

This level of coordination assures that the reader can have a level of confidence in the relevance and accuracy of the information far exceeding than that generally found on the World Wide Web. Accessibility is also a priority and for this reason each entry includes a glossary of important terms and a concise definition of the subject. In addition, we are pleased that the mathematical portions of our Encyclopedia have been selected by Math Reviews for indexing in MathSciNet. Also, ACM, the world's largest educational and scientific computing society, recognized our *Computational Complexity: Theory, Techniques, and Applications* book, which contains content taken exclusively from the *Encyclopedia of Complexity and Systems Science*, with an award as one of the notable Computer Science publications. Clearly, we have achieved prominence at a level beyond our expectations, but consistent with the high quality of the content!

Palm Desert, CA, USA
June 2022

Robert A. Meyers
Editor-in-Chief

Volume Preface

The field of statistical and nonlinear physics combines the exceedingly powerful machinery of statistical mechanics with that of nonlinear dynamics to create a highly interdisciplinary and exciting area of research. Rooted in equilibrium statistical physics, the field has evolved to encompass and emphasize the emergence of collective behavior in systems that are near and very far from equilibrium. It is a field in rapid evolution, with a constantly changing focus and a rapidly expanding realm of application.

This volume provides a modern perspective on statistical and nonlinear physics. At the heart of this subject is the exploration of collective behavior that emerges from the interactions of a large number of entities ranging from the atomic scale to objects that are macroscopic in size such as flocks of birds. The phenomena that emerge at scales involving a multitude of interacting objects are far richer than that of a few. A fundamental idea that anchors the field is that thermal motion allows the exploration of a free-energy landscape, even in systems that are driven out of equilibrium, or whose dynamics become arrested. Recent research has uncovered phenomena where this paradigm is violated strongly, and new paradigms have begun to emerge. The chapters in this volume cover both the classical and the newly emerging ideas that are continually propelling the field in new directions.

Rigidity and flow in disordered solids such as glasses, gels, and frictional granular materials is a significant focus of this second edition. Primarily because this area has experienced a paradigm shift in recent years. This volume also highlights recent developments in systems with extremely complex flows such as those encountered in the atmosphere or flows in geometries that constrict the motion severely. The application of statistical and nonlinear physics to complex networks has also been covered in this volume. These newer subjects appear side by side with core areas of the field in order to provide the reader with a comprehensive picture of the current status of the field.

The editor wishes to thank all the authors for their generosity in providing valuable and timely contributions as well as their thoughtful attention in their presentations to the needs of the readers of this volume. The editor deeply

appreciates the help and support of the entire publishing team through the long process of assembling the material and shepherding the volume through the production process.

Waltham, MA, USA
June 2022

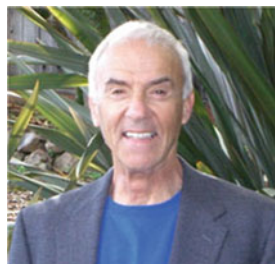
Bulbul Chakraborty
Volume Editor

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About the Editor-in-Chief



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Biography

Dr. Meyers was manager of Energy and Environmental Projects at TRW (now Northrop Grumman) in Redondo Beach, CA, and is now president of RAMTECH Limited. He is coinventor of the Gravimelt process for desulfurization and demineralization of coal for air pollution and water pollution control and was manager of the Department of Energy project leading to the construction and successful operation of a first-of-a-kind Gravimelt Process Integrated Test Plant. Dr. Meyers is the inventor of and was project manager for the DOE-sponsored Magnetohydrodynamics Seed Regeneration Project which has resulted in the construction and successful operation of a pilot plant for production of potassium formate, a chemical utilized for plasma electricity generation and air pollution control. He also managed TRWefforts in magnetohydrodynamics electricity generating combustor and plasma channel development. Dr. Meyers managed the pilot-scale DoE project for determining the hydrodynamics of synthetic fuels. He is a coinventor of several thermo-oxidative stable polymers which have achieved commercial success as the GE PEI, Upjohn Polyimides, and Rhone-Poulenc bismaleimide resins. He has also managed projects for photochemistry, chemical lasers, flue gas scrubbing, oil shale analysis and refining, petroleum analysis and refining, global change

measurement from space satellites, analysis and mitigation (carbon dioxide and ozone), hydrometallurgical refining, soil and hazardous waste remediation, novel polymers synthesis, modeling of the economics of space transportation systems, space rigidizable structures, and chemiluminescence-based devices.

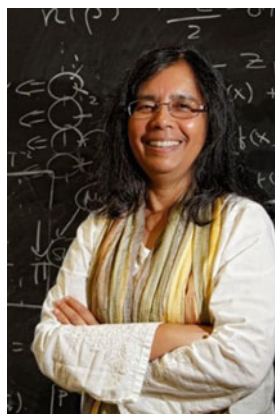
He is a senior member of the American Institute of Chemical Engineers, member of the American Physical Society, and member of the American Chemical Society and has served on the UCLA Chemistry Department Advisory Board. He was a member of the joint USA-Russia working group on air pollution control and the EPA-sponsored Waste Reduction Institute for Scientists and Engineers.

Dr. Meyers has more than 20 patents and 50 technical papers in the fields of photochemistry, pollution control, inorganic reactions, organic reactions, luminescence phenomena, and polymers. He has published in primary literature journals including *Science* and the *Journal of the American Chemical Society*, and is listed in *Who's Who in America* and *Who's Who in the World*.

Dr. Meyers' scientific achievements have been reviewed in feature articles in the popular press in publications such as The New York Times Science Supplement and *The Wall Street Journal* as well as more specialized publications such as *Chemical Engineering* and *Coal Age*. A public service film was produced by the Environmental Protection Agency on Dr. Meyers' chemical desulfurization invention for air pollution control.

Dr. Meyers is the author or editor-in-chief of a wide range of technical books including the *Handbook of Chemical Production Processes*; the *Handbook of Synfuels Technology*; the *Handbook of Petroleum Refining Processes*, now in fourth edition; the *Handbook of Petrochemical Production Processes* (McGraw-Hill), now in a second edition; the *Handbook of Energy Technology and Economics*, published by John Wiley & Sons; *Coal Structure*, published by Academic Press; and *Coal Desulfurization* as well as the *Coal Handbook* published by Marcel Dekker. He served as chairman of the advisory board for *A Guide to Nuclear Power Technology*, published by John Wiley & Sons, which won the Association of American Publishers Award as the best book in technology and engineering. He also served as editor-in-chief of three editions of the Elsevier *Encyclopedia of Physical Science and Technology*. Most recently, Dr. Meyers serves as editor-in-chief of the *Encyclopedia of Analytical Chemistry* as well as *Reviews in Cell Biology and Molecular Medicine* and a book series of the same name both published by John Wiley & Sons. In addition, Dr. Meyers currently serves as editor-in-chief of two Springer Nature book series, *Encyclopedia of Complexity and Systems Science* and *Encyclopedia of Sustainability Science and Technology*.

About the Volume Editor



Bulbul Chakraborty is the Enid and Nate Ancell Professor of Physics at Brandeis University. Her research focuses on theory of soft condensed matter. She obtained her doctorate from Stony Brook University with a thesis on superconductivity. Her early work focused on strongly correlated electronic systems, including high T_c superconductors. Her recent research has focused on developing a statistical mechanics framework for granular media and other disordered systems that are non-thermal. She is a fellow of the American Association for the Advancement of Science and the American Physical Society.

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Statistical and Nonlinear Physics: Introduction

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The “Statistical and Nonlinear Physics” section of the second edition of *Encyclopedia of Complexity and Systems Science* presents a combination of entries that highlight new developments in the field and foundational ones that provide the grounding needed to master the essence of this field that intersects physics, mathematics, computer science, and biology. This encyclopedia section is intended to be a resource for junior scientists entering the field and established scientists branching out into new areas.

Rooted in equilibrium statistical physics and nonlinear dynamics, the subject matter of this book has evolved to encompass a vast array of emergent phenomena in systems that can be near equilibrium or very far from it, dominated by thermal fluctuations or completely athermal but driven externally. A hallmark of the field is that it is constantly in a state of evolution and expansion of focus.

The singular objective of statistical and nonlinear physics is to describe collective behavior that emerges from the interactions of a large number of degrees of freedom. The building blocks, entities that form the “collective,” range from the atomic scale to objects that are macroscopic in size. The traditional approach is based on the prescription of interactions between the building blocks, which are then “coarse-grained” to lead to effective theories that describe phenomena that occur on length and time scales that are large compared to the building blocks. The phenomena that emerge at these scales are far richer than that of a few: The collective is not just a sum of its parts. After all, phase transitions and broken symmetry are defined only at these scales. Unlike fundamental field theories in physics that describe the behavior of the

universe at its smallest scales, the beauty of statistical and nonlinear physics lies in the “effective” field theories that define it. Classical examples range from the Navier-Stokes equations describing fluids to the theory of elasticity of solids.

Entries on subjects that have remained at the core of the discipline have been updated as needed from the first edition. This volume provides an excellent introduction to the subject and demystifies the emergence of collective, novel behavior from many strongly interacting units (see ► [“Complex Systems and Emergent Phenomena”](#)). The volume also explores the fascinating field of driven disordered media which unifies phenomena ranging from earthquakes to disordered magnets where the physical features are dominated by the driving of an internal elastic membrane or interface through a medium that “pins” it at random spatial positions (see ► [“Disordered Elastic Media”](#) and ► [“Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems”](#)). There is a host of other entries in these core areas that provide the reader with the essential tools of the trade.

The emergence of rigidity in disordered solids such as glasses, gels, and frictional granular materials is a significant focus of this second edition, primarily because this area has experienced a paradigm shift in recent years. There are entries that focus on the fundamental theoretical ideas that are needed to understand the response of disordered solid to external stresses (see *Topological Mechanics*). The quintessentially hard problem of the glass transition is also tackled (see ► [“Glasses and Aging, A Statistical Mechanics Perspective on”](#)). The emergence of rigidity and stress heterogeneities in granular solids and gels is discussed (see ► [“Rigidity Percolation and Frictional Jamming”](#) and ► [“Stress Localization in Soft Particulate Gels”](#)), as well as the yielding and failure of such solids (see ► [“Nonlinear Mechanics of Colloidal Gels: Creep, Fatigue, and Shear-Induced Yielding”](#)).

Another area of research that this second edition focuses on are complex flows (see ► [“Dense](#)

Active Matter,” ► “Statistical Mechanics of Clogging,” and ► “Fluid Dynamics in Clouds”). These add to the techniques and extend the principles presented in the entries on ► “Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence” and ► “Granular Flows,” which have been updated from the first edition.

The study of Networks has become integral to statistical mechanics since the publication of the first edition. The discussion from the first edition

(see ► “Networks: Structure and Dynamics”) is now augmented by a more focused discussion of an aspect of Network theory that is being increasingly employed to analyze the relation between the structure and function of networks in complex systems (see ► “Centralities in Complex Networks”).

We hope that this collection of entries will be a useful resource to the existing community of scientists engaged in statistical and nonlinear physics research, and to anyone wishing to enter this field.

Complex Systems and Emergent Phenomena

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Article Outline

Glossary
Definition of the Subject
Introduction
Equilibrium Averages
The Two-Dimensional *XY*-Model
Lack of Ordering in Two Dimensions
Vortex Unbinding
The Vortex Unbinding Transition in Other Systems
Non-Equilibrium Systems
1/f Fluctuations: A Langevin Approach
Self-Organized Structure Formation: Ant Trails
Summary and Future Directions
Bibliography

Glossary

Correlations is the degree, to which events at different positions and at different times depend on or influence each other, is measured by correlation functions. If two events are statistically independent, the correlation between them is zero. The opposite is not necessarily the case, but one will often expect that if correlations decay, the mutual dependence does likewise.

Correlation function describes correlations between two quantities and depends on their separation in time and space.

Complex systems consist of a large number of interacting components. The interactions give

rise to emergent hierarchical structures. The components of the system and properties at systems level typically change with time. A complex system is inherently open and its boundaries often a matter of convention.

Equilibrium In statistical mechanics the prototype equilibrium system consists of a “small” system in thermal contact with another system, the latter being big enough to act as a heat bath. A heat bath is defined as a system so big that when it exchanges energy with the small system the temperature of the heat bath remains the same. The statistical properties of equilibrium systems are independent of time.

Generalized rigidity is a term introduced by P.W. Anderson (1984) to describe the situation, when a many component system acts as a globally connected unit, in the sense that if one apply a force at one point, the effect can be transmitted across the system. Ice has rigidity, if we push at one point, the entire piece of ice will start moving. If the ice, on the other hand melts to water, a force applied locally will only have an effect locally.

Hamiltonian expresses the energy of a system as a function of the degrees of freedom, in terms of which the system is defined at the considered level of description. Emergence in physical systems can sometimes be understood in terms of lumping degrees of freedom, in the Hamiltonian, together in sets of effective degrees of freedom, e. g. the center of mass of a solid body.

Non-equilibrium systems is a term used to describe any system that is not in equilibrium. Needless to say this is a characterization of limited value, since there are many very different types of systems included in this category.

Order parameter is a quantity that allows one to discriminate between two phases of a physical system. The order parameter changes from zero to non-zero as one passes from one phase to the other. To identify the relevant order parameter is often non-trivial and, in itself, a first important step.

Renormalization group analysis is a systematic mathematical procedure that enables a derivation of the emergent behavior at the macroscopic systems level. The behavior at long length and time scales is obtained from the underlying microscopic short length scales and fast dynamics.

Statistical mechanics seeks to understand how properties at systems level emerge from the level of the system components and their interactions. This often involves the application of probability theory, and a number of mathematical techniques. Throughout, we draw a distinction between statistical mechanics and statistical physics. The latter is mainly concerned with the microscopic foundation of thermodynamics and, e. g., phenomena such as phase transitions and superconductivity.

Definition of the Subject

Matter in the universe is organized in a hierarchical structure. At the bottom (if there is one) we have elementary particles, atoms and molecules from which we get macro molecules like proteins and DNA, these are the building blocks of organelles, which together form the cells. From cells we get organs, which put together form organisms: animals and plants of a great variety of species. One level of structure emerges from the level below. Is it possible to scientifically describe, let alone, predict emergence. Sometimes emergence is described as a phenomena beyond analysis. The perplexity with which this concept is sometimes met, is well illustrated by the following quote from a recent call for participation in a meeting, held by the British research council EPSRC, to look at ways to explore emergence in complex systems. Emergence is described in the following words: “For the first time since the enlightenment in the western tradition we have started to understand that there are non-causal systems in which some things just “are”. The concept of emergence by which patterns of possibility arise through interactions of agents over time, accepts that even with the same starting conditions the same pattern would not necessarily

repeat.” Another attitude is represented by Lord Roberts May’s statement in a recent lecture that “when people say something is an emergent property, it just means they don’t understand the phenomena”.

In this brief article we will argue that emergence is neither an empty concept nor a mysterious non-causal enigma. On the contrary, emergence is central to scientific enquiry. Emergence occurs when many components interact and combine to form an identifiable system. In philosophy this is the observation that quantitative changes accumulate and give rise to new qualitative changes. A proposition that can be traced from the ancient Greek philosophers through Hegel to Dialectical Materialism. In physics Phil Anderson famously summed the fact that new levels of organization need new types of description, up in the phrase “More is Different” (Anderson 1972). By following the tradition of statistical mechanics it is sometimes possible to reduce significantly the confusion surrounding what emergence is, and how it can be investigated and described. Kenneth Wilson got the 1982 Nobel prize for his Renormalization Group theory, which is a particular beautiful method for extracting certain emergent properties with great mathematical detail and precision (Wilson 1982).

Introduction

Statistical mechanics is concerned with the interaction of many components. From interactions between the components at one given level the aim is to understand the collective coherent behavior, which emerges as many components are put together. It is through the interactions of the components at one level that the next level emerges. We consider a collection of *interacting* atoms and the outcome is, say, a transistor. In some cases the microscopic details of the properties of the *individual* building blocks are not so crucial. It happens that the collective behavior is controlled by general properties of the *interactions* between the components more than by the intrinsic properties of the components. A number of methods have been developed to bridge the gap

between the individual components comprising a system and the collective whole. This often involves predictions of the asymptotic behavior at long distances and at long times. In particular the philosophy and technique of the Renormalization Group have been successful in a number of cases in doing this. Many other approaches exist, some in which a coarse grained description is sought similar to the one used in fluid dynamics, other times the collective systems level behavior is generated by use of Individual Based Agent models typically simulated on computers. The latter method goes beyond traditional statistical mechanics, nevertheless it is reasonable to consider simulations of agent based models as part of statistical mechanics since they are very similar in spirit to traditional statistical mechanics simulations starting from the microscopic degrees of freedom, as e. g. extensively done for the celebrated Ising model used in studies of magnetic systems, melting and many other phenomena.

In this article we will discuss a number of examples of how statistical mechanics is able to deal with emergent phenomena. Our first example is from the theory of equilibrium properties of magnetic materials. In the model the microscopic magnetic moments – or spin – combine to form macroscopic coherent vortices. The vortices are bound in pairs at low temperature. When the temperature is increased, the biggest pairs are able to unbind, or fall apart. This is a subtle collective effect caused by the smaller pairs weakening the binding force between the vortices in the biggest pairs. We use this case to describe in some detail how the statistical mechanics formalism of Boltzmann and Gibbs allows us to identify the macroscopic excitations. These macroscopic excitations are what constitute the macroscopic “components” of the system, once they are identified we can calculate the unbinding of the vortex pairs. This discussion focuses on spatial aspects. The mathematical description developed from this model has applications to a range of very different phenomena, such as melting, superconductivity, super fluidity, electrical charges in two-dimensional space and crystal growth. This is a good typical example of how the mathematical formalism of statistical mechanics is able to

deliver understanding, and a description, transcending the particular and unify apparently disconnected phenomena.

Many-component systems also often exhibit emergent temporal behavior that is caused by the interactions and ensuing collective motion of the components. For example, one typically see very persistent correlations, or long time memory, in the macro-dynamics of many-component systems. A particular version of this phenomena is called $1/f$ fluctuations, and we explain below what this is, and how it is related to long time correlations or long memory effects. To make the discussion concrete we will present the details of a very simple model of diffusing particles. The model might be related to motorway traffic.

To go beyond models taken from physics we will finish by a discussion of models inspired by the observed collective behavior of social insects. Aspects of trail formation and mound building of ants and termites have been reproduced in computer simulations. Often the models consider “agents” with a tendency to perform random walks and picking up and laying down material. The agents deviate from random walking when they come across traces of smell – pheromones – laid down by other ants. This indirect interaction can lead to the formation of surprisingly intricate structures of trails and mounds.

Since essentially any activity within statistical mechanics is concerned with a description of emerging phenomena a very large literature exists and we list here only a few books of particular relevance to the view point of the present article (Anderson 1984; Reif 1965; Shang-Keng 1985; Kadanoff 2000; Binney et al. 1992; Nelson 2002; Chaikin and Lubensky 1995; Tinkham 2004; Sornette 2004; Camazine et al. 2001; Solé and Goodwin 2000) and some more specialized papers as we go along.

Equilibrium Averages

To describe how statistical mechanics is able to identify structures emerging at the macroscopic level we briefly recall how macroscopic (or systems level) quantities are obtained through

averaging procedures. The reason equilibrium systems can be analyzed in particular detail is that the situation, where the systems of interest can be considered as in thermal equilibrium with a heat bath, allows for the determination of the probability weights of the individual micro-states. One starts out with the following fundamental hypothesis concerning isolated or closed systems:

- **Micro Canonical Ensemble.** For a closed system it is assumed that *all* micro-states, consistent with the macroscopic constraints, occur with *equal* probability.

The macroscopic constraints can, for example, be the total energy E (which is constant for a closed system) and the volume V . Denote by $\Omega(E, V)$ the total number of micro-states possible under these constraints. Meaning the components or particles of the system have to be located within the given volume V , and that when we add all the energies of the particles the sum must equal E . The probability $p(s)$ that the system is in a particular state s is then

$$p(s) = \frac{1}{\Omega(E, V)}. \quad (1)$$

Closed systems are not very interesting in the sense that one is unable to interact with them. A much more interesting situation is when the system $\mathbf{S}$ under consideration is brought in contact with a heat bath $\mathbf{B}$ or heat reservoir. The heat bath is a system so big that even when it exchanges energy with the small system of experimental interest, the heat bath remains unchanged. Say a cup of tea in contact with the Pacific Ocean. The heat bath is characterized by its temperature T . We can now use the fundamental hypothesis above to determine the probabilistic weights for the states of $\mathbf{S}$. Since the combined system $\mathbf{B} + \mathbf{S}$ is closed the weights for the combined system is given by the Micro Canonical Ensemble, i.e. all microstates of the combined system are equally likely. The number of micro-states for the combined system of total energy $E_{\text{Tot}} = E_{\mathbf{B}} + E_{\mathbf{S}}$ will be a product

$$\Omega_{\text{Tot}}(E_{\text{Tot}}) = \Omega_{\mathbf{B}}(E_{\mathbf{B}})\Omega_{\mathbf{S}}(E_{\mathbf{S}}). \quad (2)$$

Here one neglects the interactions between the heat bath and the system. Now focus on one particular micro-state s of $\mathbf{S}$ of energy E_s . Since we have a particular state, s , in mind we have $\Omega_{\mathbf{S}}(s) = 1$. This state can be combined in many ways with states of the bath $\mathbf{B}$ as long as those fulfill the constraint $E_{\text{Tot}} = E_{\mathbf{B}} + E_s$. So the probability, $p(s)$, for finding the system $\mathbf{S}$ in s , when $\mathbf{S}$ is in equilibrium with the bath, is proportional to $\Omega_{\mathbf{B}}(E_{\text{Tot}} - E_s)$. Namely

$$p(s) = \frac{\Omega_{\mathbf{B}}(E_{\text{Tot}} - E_s)}{\sum_{\text{state}} \Omega_{\mathbf{B}}(E_{\text{Tot}} - E_{\text{state}})}, \quad (3)$$

the denominator ensures normalization. In order to introduce the temperature into the mathematical formalism it turns out that we should consider the logarithm of $p(s)$. We have

$$\begin{aligned} \ln [p(s)] &= \text{constant} + \ln [\Omega_{\mathbf{B}}(E_{\text{Tot}} - E_s)] \\ &= \text{constant} + \ln [\Omega_{\mathbf{B}}(E_{\text{Tot}})] \end{aligned} \quad (4)$$

$$- \frac{\partial \ln [\Omega_{\mathbf{B}}(E_{\text{Tot}})]}{\partial E_{\text{Tot}}} E_s \quad (5)$$

$$= \text{constant} - \frac{1}{k_{\text{B}}T} E_s. \quad (6)$$

Here we Taylor expanded to linear order to obtain the first equality. The second equality follows, because it can be shown by use of the first and second law of thermodynamics that the temperature is given by

$$\frac{1}{k_{\text{B}}T} = \frac{\partial \ln [\Omega_{\mathbf{B}}(E_{\text{Tot}})]}{\partial E_{\text{Tot}}}. \quad (7)$$

This is obtained in the following way. The first and second law of thermodynamics lead to the following thermodynamic identity $dE = TdS - pdV$ where the entropy $S = k_{\text{B}} \ln[\Omega(E)]$. Since the thermodynamic identity takes the form of an exact differential we conclude that $\partial E/\partial S = T$ from which Eq. (7) follows. We now conclude

$$p(s) = \frac{e^{-\frac{E_s}{k_B T}}}{Z}, \quad (8)$$

where the constant Z is obtained from the normalization condition

$$\sum_{\text{states}} p(s) = 1, \quad (9)$$

to be given by

$$Z = \sum_{\text{states}} e^{-\frac{E_s}{k_B T}}. \quad (10)$$

We conclude that the probabilistic weights, needed to calculate the average macroscopic behavior of a system in contact with a heat bath at temperature T , is given by the (Boltzmann) weights in Eq. (8). And we mention that a large number of average quantities can be calculated from the sum in Eq. (10). This important sum is called the *partition function* or partition sum. Some states, or configurations of the microscopic degrees of freedom, will contribute more to the partition sum than others, such configurations can sometimes be identified as macroscopic collective excitations. These may possess a degree of robustness and stability and can in such cases be identified as macroscopic emergent objects with specific properties that can be considered essential building blocks. Perhaps it is instructive to have the following picture in mind. Think of a pool table. To describe the motion of the balls we can either follow the trajectories of all the individual molecules making up 15 colored balls or we can notice that some of the molecules move together in a coordinated way and thereby form each of the 15 balls. We can therefore instead simply follow the trajectories of the center of mass (COM) of each of the balls. Obviously we lose a lot of information since we can't go from the COM of the balls to the motion of all the molecules; whereas we can drive the COM motion if we know the motion of all the molecules. Hence we note that emergence involves a loss of information. We will discuss in detail an important and illustrative example in the next section.

The Two-Dimensional XY-Model

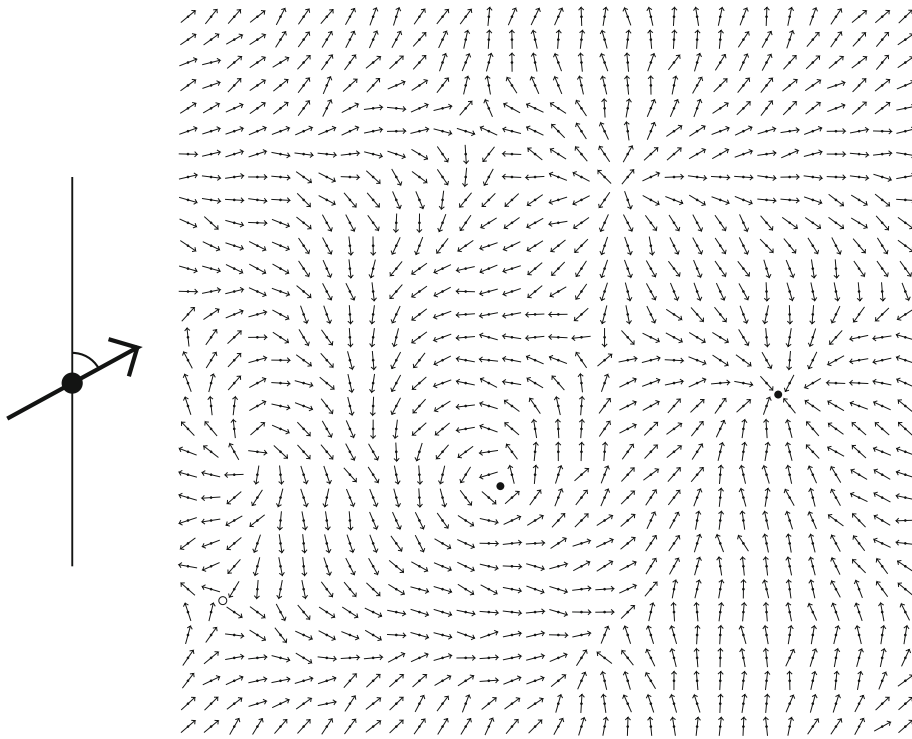
Here we describe how the averaging procedure described in the previous section can be structured in a way that allows the introduction of new effective collective degrees of freedom. These describe macroscopic excitations created by the coherent motion of a huge number of microscopic variables. When the collective degrees have been identified information concerning the detailed motion of the microscopic variables can be neglected, and one is in this way able to reduce the computational effort needed and at the same time identify the essential emergent structures. A particular clear example of this procedure consists of the physics of systems modeled by the so-called two-dimensional *XY*-model.

We start our discussion by considering the formation of vortices in the sea of two-dimensional magnetic moments. The individual microscopic magnetic moments sit on the sites of a two-dimensional square lattice and the direction of the moments are confined to two dimensions, see Fig. 1 (A beautiful online interactive simulation can be found on Hans Weber's web page at <http://www.mt.luth.se/~weber/>). Each magnetic moment can be thought of as a magnetic needle, or an arrow, confined to two dimensions and pointing in a specific direction described by the angle θ . The magnetic moment number i is given by the vector $\mathbf{S}_i = (\cos(\theta_i), \sin(\theta_i))$.

We will use it as our reference model. We think of the model as consisting of planar rotors of unit length arranged on a two-dimensional square lattice. The Hamiltonian of the system is given by

$$\begin{aligned} H &= -J \sum_{\langle i, j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \\ &= -J \sum_{\langle i, j \rangle} \cos(\theta_i - \theta_j). \end{aligned} \quad (11)$$

Here J is the coupling constant between the magnetic moments, $\langle i, j \rangle$ denotes summation over all nearest neighbor sites in the lattice, and θ_i denotes the angle of the rotor on site i with respect to some (arbitrary) polar direction in the



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Fig. 1 Rotor configuration of the XY-model. Vortices (black circle) and anti-vortices (white circle) are clearly seen. The configuration is neutral, i.e. there is an equal

number of vortices and anti-vortices; but only one white circle is indicated. The reader may find it amusing to try to locate the missing anti-vortex

two-dimensional vector space containing the rotors.

We shall see below how the components, the rotors, work together to form certain collective coherent structures: topological defects or topological charges. In Fig. 1 these excitations are depicted. Each consists of a whirl or vortex in the configuration of the rotors. There are vortices of opposite sign. As one moves around in a positive direction along a contour encircling the center of a vortex (black circle) the rotors perform a full rotation in the positive direction as well. When we move around one of the anti-vortices (white circle) in a similar way, the rotors undergo a full rotation in the negative direction. Although these charges are here seen as arising from rotors or magnetic moments, the impressive fact is that these topological charges also represent Coulomb charges in two dimensions, or dislocations in two-dimensional

crystals, or vortices in two-dimensional superconductors or a large number of other collective excitations. The interaction between the topological charges depends in all cases logarithmically on the spatial separation and this leads to some very general collective behavior, most spectacular the logarithmic dependence on separation causes a certain type of phase transition: the Kosterlitz–Thouless transition (Kosterlitz and Thouless 1973).

If we assume that the direction of the rotors varies smoothly from site to site, we can approximate $\cos(\theta_i - \theta_j)$ by the first two terms $1 - 1/2(\theta_i - \theta_j)^2$ in the Taylor expansion of $\cos$. The sum over the nearest neighbors corresponds to the discrete Laplace operator, which we can express in terms of partial derivatives through $\theta_i - \theta_j = \partial_x \theta$ for two sites i and j which differs by one lattice spacing in the x -direction. This leads to the continuum Hamiltonian

$$H = E_0 + \frac{J}{2} \int \mathbf{dr} (\nabla \theta)^2. \quad (12)$$

Here $E_0 = 2JN$ is the energy of the completely aligned ground state of N rotors.

The thermodynamics of the system is obtained from the partition function

$$Z = e^{-\beta E_0} \int D[\theta] \exp \left\{ -\beta \frac{J}{2} \int \mathbf{dr} (\nabla \theta)^2 \right\}, \quad (13)$$

a functional integral over all possible configurations of the director field $\theta(\mathbf{r})$. Not all configurations will be of the same importance. By focusing on the terms in the sum that contribute most, we can identify the configurations that may be used as building blocks at the next level of description. Since the energy appears in the exponential with a negative sign in front, the most significant contributions will be those with the smaller energy – thus we have to pick out the local minima. We therefore divide the integral over $\theta(\mathbf{r})$ into a sum over the local minima θ_{vor} of $H[\theta]$ plus fluctuations θ_{sw} around the minima

$$Z = e^{-\beta E_0} \sum_{\theta_{\text{vor}}} \int D[\theta_{\text{sw}}] \exp \left\{ -\beta (H[\theta_{\text{vor}}] + \frac{1}{2} \int \mathbf{dr}_1 \int \mathbf{dr}_2 \theta_{\text{sw}}(\mathbf{r}_1) \frac{\delta^2 H}{\delta \theta(\mathbf{r}_1) \delta \theta(\mathbf{r}_2)} \theta_{\text{sw}}(\mathbf{r}_2)) \right\}. \quad (14)$$

The field configurations corresponding to local minima of H are solutions to the extremal condition

$$\frac{\delta H}{\delta \theta(\mathbf{r})} = 0 \Rightarrow \nabla^2 \theta(\mathbf{r}) = 0. \quad (15)$$

There are two types of solutions to this equation. The first consists of the ground state $\theta(\mathbf{r}) = \text{constant}$. The second type of solutions consist of vortices in the director field (see Fig. 1) and are obtained by imposing the following set of boundary conditions on the circulation integral of $\theta(\mathbf{r})$:

- 1) For all closed curves encircling the position $\mathbf{r}_0$ of the center of the vortex

$$\oint \nabla \theta(\mathbf{r}) \cdot \mathbf{dl} = 2\pi n, \quad n = 1, 2, \dots \quad (16)$$

- 2) For all paths that don't encircle the vortex position $\mathbf{r}_0$

$$\oint \nabla \theta(\mathbf{r}) \cdot \mathbf{dl} = 0. \quad (17)$$

Condition 1) imposes a singularity in the director field. Note the circulation integral *must* be equal to an integer times 2π since we circle a closed path and therefore $\theta(\mathbf{r})$ has to point in the same direction after traversing the path as it did when we started.

We can estimate the energy of a vortex in the following way. The problem is spherical symmetric, hence the vortex field θ_{vor} must be of the form $\theta(\mathbf{r}) = \theta(r)$. The dependence on r can be found from Eq. (16). We calculate the circulation integral along a circle of radius r centered at the position $\mathbf{r}_0$ of the vortex

$$2\pi n = \oint \nabla \theta(\mathbf{r}) \cdot \mathbf{dl} = 2\pi r |\nabla \theta|. \quad (18)$$

We solve and obtain $|\nabla \theta(r)| = n/r$. Substitute this result into the Hamiltonian Eq. (12)

$$E_{\text{vor}} - E_0 = \frac{J}{2} \int \mathbf{dr} [\nabla \theta(\mathbf{r})]^2 \quad (19)$$

$$= \frac{Jn^2}{2} \int_0^{2\pi} d\phi \int_a^L r \mathbf{dr} \frac{1}{r^2} \quad (20)$$

$$= \pi n^2 J \ln \frac{L}{a}. \quad (21)$$

Here a denotes the lattice constant and L is the linear size of the considered lattice. The circulation condition Eq. (16) creates a distortion in the phase field $\theta(\mathbf{r})$ that persists infinitely far from the center of the vortex. $|\nabla \theta|$ decays only as $1/r$ leading to a logarithmic divergence of the energy. Hence we need to take into account that the

integral over r in Eq. (20) is cut-off for large r -values by the finite system size L and for small r -values by the lattice spacing a . We recall that our continuum Hamiltonian is an approximation to the lattice Hamiltonian in Eq. (11). A vortex with the factor n in Eq. (16) larger than one is called multiple charged. We notice that the energy of the vortex is quadratic in the charge. In a macroscopically large system even the energy of a single charge vortex will be large, and therefore we do not expect individual vortices to be thermally induced.

Consider now a pair consisting of a single charged vortex and a single charged anti-vortex. When we encircle the vortex, we pick up $\oint d\mathbf{l} \cdot \nabla \theta = 2\pi$ and when we encircle the anti-vortex, we pick up $\oint d\mathbf{l} \cdot \nabla \theta = -2\pi$. Hence, if we choose a path large enough to enclose both vortices, we pick up a circulation of the phase equal to $2\pi + (-2\pi) = 0$. I.e. the distortion of the phase field $\theta(\mathbf{r})$ from the vortex-anti-vortex pair is able to cancel out at distances from the center of the two vortices large compared to the separation R between the vortex and the anti-vortex, see Fig. 1. This explains why the energy of the vortex pair is of the form (Cataudella and Minnhagen 1990; Weber and Jensen 1991; Minnhagen and Olsson 1991).

$$E_{2\text{vor}}(R) = 2E_c + E_1 \ln(R/a). \quad (22)$$

Where E_c is the energy of a vortex core and E_1 is proportional to J . In detail, the phase field $\theta_{2\text{vor}}(\mathbf{r})$ of a vortex located at $\mathbf{r} = (-a, 0)$ and an anti-vortex located at $\mathbf{r} = (a, 0)$ is given by (Cataudella and Minnhagen 1990).

$$\theta_{2\text{vor}}(\mathbf{r}) = \arctg\left(\frac{2ay}{a^2 - r^2}\right). \quad (23)$$

Significant aspects of the macroscopic behavior of the XY -model can be understood by treating the vortices as particles characterized by their position and their charge and ignoring the underlying sea of rotors. Indication of this follows from the expression for the energy of a pair of vortices in Eq. 22. This energy is given in terms of the

relative position of the two vortices, no reference is needed to the microscopic rotor field given in Eq. 23. The pairs of vortices have dramatic effects on the macroscopic behavior of the XY -model. At low temperature the vortices are organized in fairly small bound pairs, as the temperature is increased and more thermal energy is available the separation between paired up vortices grow and at a certain temperature the pairs break apart with the effect that the individual vortices now can move freely around as they are no longer kept in check by their partner of the opposite charge. The result is the Kosterlitz–Thouless transition which manifests itself in various ways in different realizations of the XY -model. Before we discuss this transition we will look at the average ordering of the rotors. This quantity – the magnetization – is usually able to monitor if a dramatic change in the macroscopic behavior occurs as a function of temperature. But not so in the 2d XY -model. To understand this makes it clearer how important it is to identify correctly the emergent excitations of a many component system.

Lack of Ordering in Two Dimensions

In order to highlight the peculiarity of two dimensions we consider the d -dimensional XY -model. We imagine a d -dimensional cubic lattice. Each lattice site contains a planar rotor or a phase. In the continuum limit the Hamiltonian is still given by Eq. (12) except the integral over $\mathbf{r}$ is now a d -dimensional integral and therefore the factor J is replaced by Ja^{2-d} . The average size of the projection of the rotors along, say, the x -direction in $\mathbf{S}$ space, i.e. the magnetization, is

$$\langle S_x \rangle = \langle \cos \theta(\mathbf{r}) \rangle \quad (24)$$

$$= \langle \cos \theta(0) \rangle. \quad (25)$$

Note that we might as well have chosen the y -direction. The model is isotropic and the x and the y directions are equivalent. When $\langle S_x \rangle \neq 0$ a preferred direction is singled out in the sense that on average $\mathbf{S}$ points in the direction given by $\langle S_x \rangle$.

In this case we say that the rotor field possesses order. In contrast if $\langle S_x \rangle = 0$ we also have $\langle S_y \rangle = 0$, since the model is isotropic. The zero projection comes about because the rotors circulate around and on average point equally much in all directions. So we say that the rotor field is disordered or does not possess any ordering.

First we neglect the singular vortex contributions (which is perfectly safe at low temperature) and Fourier transform the phase field

$$\theta(\mathbf{r}) = \int \frac{d\mathbf{k}}{(2\pi)^d} \hat{\theta}(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{r}} \quad (26)$$

$$\theta(0) = \int \frac{d\mathbf{k}}{(2\pi)^d} \hat{\theta}(\mathbf{k}) \quad (27)$$

$$\int d\mathbf{r} (\nabla \theta)^2 = \int \frac{d\mathbf{k}}{(2\pi)^d} k^2 \theta(\hat{\mathbf{k}}) \hat{\theta}(-\mathbf{k}). \quad (28)$$

These equations are substituted into the expression

$$\begin{aligned} \langle S_x \rangle &= \frac{\int D[\theta] \cos(\theta(0)) e^{-\beta H}}{\int D[\theta] e^{-\beta H}} \\ &= \text{Re} \left(\frac{\int D[\theta] e^{-\beta H + i\theta(0)}}{Z} \right). \end{aligned} \quad (29)$$

After some algebra one obtains the following expression

$$\langle S_x \rangle = \exp \left(-\frac{T}{2Ja^{2-d}} S_d \int_{\pi/L}^{\pi/a} dk k^{d-3} \right). \quad (30)$$

The behavior of $\langle S_x \rangle$ is controlled by the integral

$$I(L) = \int_{\pi/L}^{\pi/a} dk k^{d-3}. \quad (31)$$

The behavior of $I(L)$ strongly depends on the dimension d . For $d < 2$ we have $I(L) \sim L^{2-d} \rightarrow \infty$ as $L \rightarrow \infty$. Hence, $\langle S_x \rangle = 0$ in the limit of

large systems for dimensions less than 2. For $d > 2$ we have that

$$I(L) \rightarrow A = \frac{1}{d-2} \left(\frac{\pi}{a} \right)^{d-2} \quad (32)$$

and therefore

$$\langle S_x \rangle = \exp \left(-\frac{S_d}{2Ja^{2-d}} AT \right) > 0. \quad (33)$$

Finally for $d = 2$ the integral $I(L)$ is logarithmically divergent $I(L) = \ln(L/a)$ which is sufficient to force $\langle S_x \rangle$ to zero for any non-zero temperature.

We conclude that there is no ordered phase according to the behavior of $\langle S_x \rangle$ at low temperature for $d \leq 2$. For $d < 2$ this means that there is no phase transition. The same was for a while thought to be the case for $d = 2$. Since the thermal motion included in the calculation of $\langle S_x \rangle$ is able to prevent a preferred direction and hence ensure $\langle S_x \rangle = 0$ for $T > 0$ including other types of excitations, such as vortices, can surely not make $\langle S_x \rangle$ different from zero. So it is safe to conclude that the rotors are unable to order along a common direction for any non-zero temperature and it was accordingly expected that a phase transition in the 2d YX -model was excluded. This conclusion was reached since in magnetic systems the average of the local magnetic moment, i.e. $\langle S_x \rangle$ is the order parameter and the phase transition takes place at the temperature where the order parameter changes from zero to a nonzero value. It turned out that by identifying the vortices as emergent collective excitations and by understanding their physical effects, a phase transition of a new kind was discovered in the 2d XY -model.

Vortex Unbinding

An indication of the importance of vortices as the temperature is increased can be obtained from the following simple and heuristic argument. We estimate the free energy of a single vortex. The Helmholtz free energy is given by the difference between the energy and the entropy multiplied by the

temperature $F = E - TS$. The energy is given by Eq. (21). We estimate the entropy from the number of places where we can position the vortex center, namely on each of the $(L/a)^2$ plaquette of the square lattice, i.e., $S = k_B \ln(L^2/a^2)$. Accordingly, the free energy is given by

$$F = E_0 + (\pi J - 2k_B T) \ln(L/a). \quad (34)$$

For $T < \pi J/2k_B$ the free energy will diverge to plus infinity as $L \rightarrow \infty$. At temperatures $T > \pi J/2k_B$ the system can lower its free energy by producing vortices: $F \rightarrow -\infty$ as $L \rightarrow \infty$. This simple heuristic argument points to the fact that the logarithmic dependence on system size of the energy of the vortex combines with the logarithmic dependence of the entropy to produce the subtleties of the vortex unbinding transition. Assume a different dependence of the energy on system size and one will either have thermal activation of vortices at all temperatures (in case $E_{\text{vor}} \rightarrow \text{const.} < \infty$) or vortices will not be activated at any temperature (in case $E_{\text{vor}} \sim (L/a)^b$ with $b > 0$). It is the logarithmic size dependence of the 2d vortex energy that allows the outcome of the competition between the entropy and the energy to change qualitatively at a certain finite temperature T_{KT} .

In reality it is not single vortices of the same sign that proliferate at a certain temperature. What happens is that the larger vortex pairs which are bound together for temperatures below T_{KT} unbind at T_{KT} . This is a collective effect that can be treated quantitatively by use of a special Renormalization Group method design by Kosterlitz (Kosterlitz 1974). The vortex pairs induced as one approaches T_{KT} disturb the phase field so much that the effective value of the vortex binding term E_1 in the vortex pair free energy, that is Eq. (22) generalized to non-zero temperature, is driven to zero for large vortex separations. In the next section we shall see in detail how this happens.

The Spin Wave Stiffness

As our concern in this article is with emergent entities, we will now briefly discuss how a focus on, and an understanding of, the vortex degrees of

freedom makes it possible to identify and describe the previously “hidden” phase transition in the 2d XY-system.

The effect of the thermally activated vortex pairs is describe by the temperature dependent *spin wave stiffness* ρ_s^R . This is an example of what Philip W. Anderson calls a generalized rigidity (Anderson 1984). The spin wave stiffness describes how much free energy it costs to apply a twist, or gradient, to the rotors (also called spins):

$$\theta(\mathbf{r}) = \theta_0(\mathbf{r}) + \mathbf{v}_{\text{ex}} \cdot \mathbf{r}, \quad (35)$$

here $\theta_0(\mathbf{r})$ is allowed to vary according to the canonical ensemble. The increase in the free energy is given by

$$F(\mathbf{v}_{\text{ex}}) - F(0) = \frac{1}{2} V \rho_s^R v_{\text{ex}}^2. \quad (36)$$

A number of comments concerning the notation are illuminating. The notation $\mathbf{v}_{\text{ex}}$ for the gradient applied to the phase field $\theta(\mathbf{r})$ has its origin in the fact that the same physics, as we describe here, applies to superfluid films and superconducting films. In these cases the field $\theta(\mathbf{r})$ is the phase of the complex order parameter, the wave function of the super-fluid. Being the phase of a quantum mechanical wave function the gradient of $\theta(\mathbf{r})$ is related to a probability current and thereby to the velocity field of the superfluid. The notation ρ_s^R is meant to remind one that this phase rigidity, is determined by the **density** of superfluid in the case of a superfluid or a superconductor. The superscript R in ρ_s^R indicates that thermal excitations renormalize the quantity. It follows immediately from the Hamiltonian in Eq. (12) that at zero temperature $\rho_s^R = J = \rho_s$. The spin wave stiffness is similar to the shear constant of a material. The shear constant determines how the (free) energy increase when a shear deformation is imposed. As temperature is increased the shear constant decreases and drops abruptly to zero when the solid melts into a liquid.

To obtain ρ_s^R one calculates the left hand side of Eq. (36). Details can be found in the wonderful book by Chaikin and Lubensky (1995). The phase field is split into two parts

$$\theta_0(\mathbf{r}) = \theta_s(\mathbf{r}) + \theta_v(\mathbf{r}), \quad (37)$$

where the first term describes smooth spin waves and the second term contains the singular vortex contribution. The free energy is obtained from $F = k_B T \ln Z$ and the partition function is given by Eq. (13). To calculate Z introduce Fourier transforms of the phase field. After quite a bit of algebra one arrives at the following simple expression

$$\rho_s^R = \rho_s - \frac{1}{2} \frac{\rho_s^2}{T} \lim_{k \rightarrow 0} \frac{\langle \hat{n}(\mathbf{k}) \hat{n}(-\mathbf{k}) \rangle_0}{k^2}, \quad (38)$$

which expresses the renormalized stiffness in terms of the correlation function of the Fourier transform of the vortex density function

$$n(\mathbf{r}) = \sum_{\alpha} n_{\alpha} \delta(\mathbf{r} - \mathbf{r}_{\alpha}), \quad (39)$$

for a collection of vortices of charge n_{α} (see Eq. (16)) with centers located at positions $\mathbf{r}_{\alpha}$. The vortices are now described entirely by their position exactly like if they were ordinary

particles. So what started out as a complex configuration in the field of rotors is now possible to treat as point particles. The effect of the extended disturbance of the rotor field is taken care of by the interaction energy between two vortices. The thermodynamic average in Eq. (38) is over the canonical ensemble with no twist imposed, hence the subscript 0. Eq. (38) can be used to determine how the spin wave stiffness behaves at large distances as a function of temperature. We will discuss how in the next section.

The KT Transition

Let us first summarize the phenomenology of the Kosterlitz–Thouless transition. As the temperature is increased more and more vortex pairs are thermally activated. This makes ρ_s^R decrease, see Eq. (38). This corresponds to a decrease in the increment of the free energy induced by a certain twist $\mathbf{v}_{\text{ex}}$. We can understand the effect from the fact that the phase field $\theta(\mathbf{r})$ becomes more and more distorted as the temperature is increased, hence the extra perturbation caused by $\mathbf{v}_{\text{ex}}$ becomes relatively less important. Quantitatively one finds

$$\rho_s^R = \begin{cases} \rho_s^R(T_{\text{KT}}^-) \left[1 + \text{const.} (T_{\text{KT}} - T)^{1/2} \right] & \text{for } T < T_{\text{KT}} \\ 0 & \text{for } T > T_{\text{KT}}. \end{cases} \quad (40)$$

Here, T_{KT} is the Kosterlitz–Thouless temperature at which vortex pairs unbind. The value of T_{KT} differs from one system to another. In the 2d XY-model $T_{\text{KT}}/J \simeq 0.893 \pm 0.002$ (Olsson and Minnhagen 1991). The remarkable thing is, that the ratio

$$\rho_s^R(T_{\text{KT}}^-)/T_{\text{KT}} = 2/\pi \quad (41)$$

is universal for all systems that undergoes a KT-transition. Since $\rho_s^R(T_{\text{KT}}^+) = 0$ Eq. (41) is referred to as the universal jump. The correlation length $\xi(T)$ behaves in a very unusual way as one approaches T_{KT} from above. We are used to a relatively slow algebraic divergence of the

correlation length as the critical temperature is approached. For the KT-transition the divergence is, however, much faster

$$\xi(T) \sim \exp \left(\frac{\text{const.}}{(T - T_{\text{KT}})^{1/2}} \right) \quad \text{for } T > T_{\text{KT}}. \quad (42)$$

Can we in a simple way understand this exponential divergence? Yes, we can. The phase field is significantly distorted by unbound vortices, since these vortices are not screened by a nearby antivortex. I.e. the phases $\theta(\mathbf{r})$ can remain correlated over distances shorter than the typical distance $D = 1/\sqrt{n_{\text{ub}}}$ between unbound vortices of density

n_{ub} (Jensen and Weber 1992). Or in other words, we expect the correlation length $\xi \sim D$. The vortices are thermally induced and therefore their density is expected to depend on the temperature through a Boltzmann factor $\exp(-E_{\text{vor}}/T)$. The situation described here is exactly what happens in the one-dimensional so-called ϕ^4 model. This model supports thermally activated solitons. The correlation length is set by the inverse of the soliton density and diverges exponentially as the temperature goes to zero (Jensen and Fogedby 1985). The same thing, in a slightly simpler version, also happens in the one-dimensional Ising model. This argument can indicate the cause of the exponential dependence of ξ . But it is no more than an indication since the exponential dependence in Eq. (42) is significantly different from a simple Boltzmann factor. This difference is due to corrective renormalization effects.

Continuous phase transitions are accompanied by divergences in thermodynamic quantities caused by the divergence of the correlation length as the critical temperature T_c is approached. The singular part of the free energy density f can be estimated as the amount of thermal energy T_c within a correlated volume ξ^d , which gives $f \sim T_c/\xi^d$. The specific heat c_V is given by the second derivative of the free energy $c_V = -T\partial^2 f/\partial T^2 \sim \partial^2 \xi^{-d}/\partial T^2$. For the KT-transition the exponential divergence of $\xi(T)$ in Eq. (42) is so rapid and occur over such a narrow temperature range that the divergence in c_V cannot be resolved in simulations or in experiment. This is another reason why the vortex unbinding transition remained unnoticed for so long. It doesn't leave any dramatic signature in the thermodynamic quantities. However, as mentioned above, the macroscopic rigidity clearly changes at the transition.

The Vortex Unbinding Transition in Other Systems

We have above mentioned that not only the XY-model exhibits the Kosterlitz–Thouless vortex unbinding transition (Minnhagen 1987). Any two-dimensional system that supports thermally

induced “charges” or topological defects that interact logarithmically will undergo this transition. The $U(1)$ symmetry of the phase field $\theta(\mathbf{r})$ of the XY-model is also present in the Ginzburg–Landau free energy of superfluids and of superconductors. The topological excitations in the case of a superfluid consist of vortices in the flow of the superfluid. Vortices like those observed when one empties a bath tub. In thin superfluid helium film such vortices destruct the superfluid phase with increasing temperature according to the scenario of the KT-transition (Ambegaokar et al. 1978, 1980).

The situation is slightly more complicated in superconductors. Because the superfluid in this case is charged (the superconducting pairs of electrons), screening effects play a role (Chaikin and Lubensky 1995; Tinkham 2004; Minnhagen 1987). However, for thin superconducting films of thickness δ the effective screening length is given by $\lambda_{\text{eff}} = \lambda^2/\delta$, which can easily become a macroscopic length. In this case the loss of superconductivity is caused by the unbinding of vortex pairs according to the KT-transition. The broken pairs can move freely when they respond to an applied electric current. As they move they cause phase slips in the superconducting order parameter. These phase slips induce a voltage drop according to the Josephson relation. The superconductor is now unable to support an electric current without a voltage drop, i.e. it is not a superconductor any longer (Kadin et al. 1983; Huberman et al. 1978; Doniach and Huberman 1979; Beasley et al. 1979).

Dislocations in two-dimensional crystals interact through the strain field. Two edge dislocations of opposite sign correspond to an extra row of atoms inserted along the line connecting the location of the two dislocation cores. The extra line of atoms produces strain and leads to an increase in the energy which is logarithmic in the separation between the two dislocations. Thus, the situation is very similar to the one encountered in the XY-model. When the dislocations unbind, free dislocations are produced. A shear applied to the system can now be accommodated by the mobile dislocations without an increase in the (free) energy. I.e., the shear constant has dropped to zero and the system is

melted. The 2d melting theory of Kosterlitz–Thouless–Halperin–Nelson–Young predicts that melting occurs in two stages. At the first stage dislocations unbind and make the shear constant drop to zero. The dislocations are topological defects, their effect on the order of the lattice are, however, not very dramatic. Before the unbinding of dislocations, the translational and the orientational order of the lattice are both described by correlation functions that depend algebraically on distance. When the dislocations unbind the translational correlation function becomes exponential but the orientational correlations remain algebraic. At a somewhat higher temperature topological defects called disclinations unbind with the effect that the orientational order becomes exponential. Details can be found in Chaikin and Lubensky (1995).

There are many other cases where the logarithmic vortex interaction and the KT-transition play a role. For instance, the shape of surfaces in three dimensions may undergo a transition from smooth to rough (Barabási and Stanley 1995). Assume that the surface energy of the two-dimensional surface is proportional to the area of the surface. And assume that the surface is defined in terms of its height $h(x, y)$ above the xy -plane, i.e. no overhangs. In other words the points on the surface have the coordinates $(x, y, h(x, y))$. The Hamiltonian for the surface is then

$$H = \sigma \int dx \int dy \sqrt{1 + (\nabla h)^2}. \quad (43)$$

Here σ is a measure of the surface tension. If the height only varies slowly as a function of (x, y) we can assume $|\nabla h| \ll 1$ and then expand the square root. In this approximation the Hamiltonian in Eq. (43) can be written as

$$H = \sigma L^2 + \frac{1}{2} \int dx \int dy (\nabla h)^2, \quad (44)$$

(L is the linear size of the system in the xy -plane) which is equivalent to Eq. (19), and we expect the same physical phenomenology to apply to the surface as we found for the XY -model.

Non-Equilibrium Systems

The Boltzmann probabilities cannot be used to calculate the macroscopic properties when we deal with situations that have no equivalence among systems in contact with a heat bath. At present there is no general procedure for the determination of the probability weights of the individual microstates. This doesn't mean that statical mechanics can't describe how macroscopic properties emerge in systems out of equilibrium. Indeed approaches of broad interest exist. Here we will briefly introduce the use of Langevin equations and algorithmic models through two concrete simplistic models. The first is inspired by the very long memory or correlation times often observed in complex systems. We will discuss slow flowing motorway traffic. The other is concerned with the emergence of self-organized structures among interacting living organisms. Specifically we will think of the formation of ant trails.

1/f Fluctuations: A Langevin Approach

In this section we describe an example of emergence in time. We will assume that interaction between the components of our system forces these to diffuse around, rather than to move around in a ballistic manner. The result is a time signal that contains very strong correlations and is characterized by what is denoted a $1/f$ power spectrum (Milotti 2008).

We want to study correlations in a time signal $f(t)$. We measure the signal again and again at two times separated by T time units. To make life simple we will *neglect* the normalization factor in the empirical averages, i.e. we don't divide by the number of terms in the sum in Eq. (45) below. A justification for this is that we are interested in the functional dependence of the correlations on the time interval T and not so much interested in the actual specific value of the correlation coefficient. Since the correlation coefficient will depend on T we talk about the correlation function. Moreover, since we are correlating the signal with itself we talk about the autocorrelation function given by:

$$\begin{aligned}
C(T) &= \sum_t [f(t) - \langle f(t) \rangle][f(t+T) - \langle f(t+T) \rangle] \\
&= \int dt [f(t) - \langle f(t) \rangle][f(t+T) - \langle f(t+T) \rangle] \\
&= \int dt [f(t) - \langle f(t) \rangle][f(t+T) - \langle f(t) \rangle].
\end{aligned} \tag{45}$$

In the last equality we made use of the fact that the average of value $f(t)$ and $f(t+T)$ are identical.

The autocorrelation function is an important object for the study of memory effects or causality effects in a signal. The correlation function is equivalent to the *power spectrum*. The power spectrum of the signal $f(t)$ is defined as

$$S_f(\omega) = |\hat{f}(\omega)|^2. \tag{46}$$

That is the absolute value squared of the Fourier transform of the signal and the power spectrum is related to the Fourier transform of the autocorrelation function:

$$S_f(\omega) = \hat{C}(\omega). \tag{47}$$

This relation explains why power spectra that approximately depend inversely proportional on the frequency

$$S_f(\omega) \propto 1/\omega^\beta, \tag{48}$$

with $\beta \simeq 1$, are of special interest (Press 1978; Weissman 1988; Grinstein et al. 1992). Namely, at a somewhat heuristic level, we can substitute Eq. (48) into Eq. (47) and then into

$$C(T) = \int_{-\infty}^{\infty} d\omega \hat{C}(\omega) e^{-i\omega T}, \tag{49}$$

to obtain

$$C(T) = \int_{-\infty}^{\infty} d\omega \omega^{-\beta} e^{-i\omega T} \tag{50}$$

$$= T^{1-\beta} \int_{-\infty}^{\infty} du u^{-\beta} e^u. \tag{51}$$

We made the substitution $u = \omega T$ and note that the integral in the above equation now is independent of T . So when $\beta \simeq 1$, the correlation function $C(T)$ depends very weakly on T meaning very slow decay of correlations. This indicates the particular interest in power spectra that approximately decays as one over the frequency – called $1/f$ noise. The way we carried the argument through is slightly dangerous due to possible divergent integrals; the conclusion is, however, sound.

Transport by Diffusion

For concreteness imagine a piece of motorway stretching from $x = -\infty$ to $x = \infty$. At $x = 0$ vehicles can enter or leave at an intersection. We will develop a model for the time evolution of the density of cars $n(x, t)$ at position x at time t . Since the cars – particles – only can leave or enter our system at $x = 0$, at all other positions, $x \neq 0$, changes during a brief time interval δ in the number of particles in a small interval $[x, x + \delta x]$ about x

$$\delta n(x, t) = n(x, t + \delta t) \delta x - n(x, t) \delta x \tag{52}$$

will be caused by a difference during the time δt between the number of particles leaving the section $[x, x + \delta x]$ at $x + \delta x$ and the number of particles entering the section at x . Let $J(x, t)$ denote the particle current (number of particles crossing the position x at time t per time unit). We can then write

$$\delta n(x, t) = J(x + \delta x, t) \delta t - J(x, t) \delta t. \tag{53}$$

Substituting Eq. (53) into Eq. (52) we obtain

$$\begin{aligned}
n(x, t + \delta t) \delta x - n(x, t) \delta x &= -J(x + \delta x, t) \delta t + J(x, t) \delta t \\
\Downarrow
\end{aligned} \tag{54}$$

$$\frac{\partial n(x, t)}{\partial t} = -\frac{\partial J(x, t)}{\partial x}. \tag{55}$$

The last equation follows in the limit $\delta x \rightarrow 0$ and $\delta t \rightarrow 0$.

This equation is exact and only assumes conservation of the particles. To obtain a closed equation for $n(x, t)$ we need to relate $J(x, t)$ to $n(x, t)$. And to do so we need to make assumptions concerning the nature of how the particles, or cars, move along the line. Let us imagine that congestion makes it impossible for cars to move freely. On the contrary assume that the drivers are forced to effectively perform random walks; i.e. diffuse along the motorway.

We emphasize that it is through this assumption that the cars, or particles, are made to interact. Here we assume that the diffusion is a result of over-crowding and interaction amongst the cars. Obviously particles might perform diffusive motion as a result of other interactions. Pollen in water diffuses because it is bombarded by large numbers of water molecules. In any case some sort of complex interaction is always responsible for diffusive motion since the particles otherwise would move around according to Newton's laws. The model might in fact be more relevant to small particles (pollen, say) suspended in a long narrow strip of water – or something else.

To model the jamming and resulting diffusive motion, we will assume that the net particle current (at coarse grained level) is from high particle density to low particle density, and linear in the density difference. We express this as

$$J(x, t) = -\gamma \frac{\partial n(x, t)}{\partial x}. \quad (56)$$

We combine Eq. (55) and Eq. (56) to obtain a closed form of dynamical equation for $n(x, t)$:

$$\frac{\partial n(x, t)}{\partial t} = \gamma \frac{\partial^2 n(x, t)}{\partial x^2}. \quad (57)$$

This is the well-known diffusion equation. It describes how inhomogeneities in the density $n(x, t)$ relaxes by diffusion. The equation describes a closed system. Next we include the particles that might be added or removed at a certain rate $g(x, t)$ at position x at time t . According to the description above we have in particular in mind that $g(x, t)$

must describe cars leaving and entering at $x = 0$. We will later return to how this particular requirement can be imposed on $g(x, t)$. We now have our final equation of motion for $n(x, t)$

$$\frac{\partial n(x, t)}{\partial t} = \gamma \frac{\partial^2 n(x, t)}{\partial x^2} + g(x, t). \quad (58)$$

This is an inhomogeneous partial differential equation and we solve it easily by Fourier transformation

$$n(x, t) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \hat{n}(k, \omega) e^{i(kx + \omega t)}. \quad (59)$$

Substitute into Eq. (58) to obtain an expression for $\hat{n}(k, \omega)$ in terms of the Fourier transform of the drive $\hat{g}(k, \omega)$

$$\hat{n}(k, \omega) = \frac{\hat{g}(k, \omega)}{i\omega + \gamma k^2}. \quad (60)$$

Now substitute Eq. (60) into Eq. (59):

$$n(x, t) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\hat{g}(k, \omega)}{i\omega + \gamma k^2} e^{i(kx + \omega t)}. \quad (61)$$

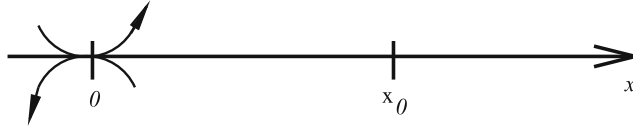
Next we want to focus on the density fluctuations at a specific position $x_0 > 0$. Therefore we define

$$N(t) \equiv n(x_0, t) - \langle n(x_0, t) \rangle_t, \quad (62)$$

where we have subtracted the temporal averaged density. We will determine the power spectrum of $N(t)$ and for this purpose need the Fourier transform

$$\hat{N}(\omega) = \int_{-\infty}^{\infty} dt N(t) e^{-i\omega t} \quad (63)$$

$$= \int_{-\infty}^{\infty} dt n(x_0, t) e^{-i\omega t} - \langle n(x_0, t) \rangle_t \int_{-\infty}^{\infty} dt e^{-i\omega t} \quad (64)$$



Complex Systems and Emergent Phenomena, Fig. 2 Cars/particles diffusing up and down a motorway stretching from $x = -\infty$ to $x = \infty$. At $x = 0$ an intersection

allows the vehicles to enter or leave the motor way. At $x = x_0$ a traffic warden is monitoring the number of vehicles, $N(t)$, in front of him

$$= \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{\hat{g}(k, \omega)}{i\omega + \gamma k^2} e^{ikx_0} - \langle n(x_0, t) \rangle_t \delta(\omega). \quad (65)$$

That is how far we can go without further assumptions concerning the nature of the drive $g(x, t)$. Since this source term is meant to represent vehicles entering and leaving at position $x = 0$ we will now use

$$g(x, t) = \delta(x)\chi(t) \Rightarrow \hat{g}(\omega) = \hat{\chi}(\omega). \quad (66)$$

We then have that for $x \neq 0$ the source $g(x, t) = 0$ and at $x = 0$ the temporal variation in the flow onto and away from the “motorway” is given by $\chi(t)$. From Eq. (65) we get

$$\hat{N}(\omega) = \hat{\chi}(\omega) \int_{-\infty}^{\infty} dk \frac{e^{ikx_0}}{i\omega + \gamma k^2}. \quad (67)$$

The power spectrum is finally calculated as the absolute value square of $\hat{N}(\omega)$

$$|\hat{N}(\omega)|^2 = \frac{|\hat{\chi}(\omega)|^2}{4\gamma\omega} e^{-\sqrt{\frac{2\omega}{\gamma}}x_0}. \quad (68)$$

The power spectrum of the density fluctuations is clearly influenced by the power spectrum of $\chi(t)$. Let us assume that vehicles enter and leave at the intersection in a totally uncorrelated manner (perhaps not a totally realistic assumption) which translates into $|\hat{\chi}(\omega)|^2 = \text{constant}$. In this case

$$|\hat{N}(\omega)|^2 \propto \frac{1}{\omega} e^{-\sqrt{\frac{2\omega}{\gamma}}x_0}. \quad (69)$$

For frequencies so small that $\sqrt{(2\omega)/\gamma}x_0 < 1$ we have $\exp(-\sqrt{(2\omega)/\gamma}x_0) \simeq 1$ and therefore

$$|\hat{N}(\omega)|^2 \propto \frac{1}{\omega} \quad \text{for } \omega < \frac{\gamma}{2x_0^2} \equiv \frac{1}{2T_{\text{diff}}}. \quad (70)$$

Where we introduced the time scale $T_{\text{diff}} = x_0^2/\gamma$. This is the characteristic time it takes for particles, undergoing diffusion with a diffusion constant γ , to move from $x = 0$ to $x = x_0$.

Very long temporal correlations, as indicated by the $1/f$ behavior of the power spectrum, is observed in very many and diverse situations: the light intensity from quasars, the ocean current, the pitch or pressure fluctuations in speech and music, the flow of traffic, the fluctuations in the resistivity of a conductor, and many more (Press 1978; Weissman 1988). Is the model we have sketched above able to explain the observed $1/f$ correlations in all these many different systems? No, probably not. Surface driven diffusion doesn't seem to be central to all these situations. The question whether a general explanation for $1/f$ exists is still an open one.

We have considered $1/f$ fluctuations here for mainly two reasons. It is a fascinating problem which is often encountered in complex systems and our discussion illustrates how one can use stochastic differential equations to go beyond equilibrium statistical mechanics to analyze temporal emergent behavior.

Self-Organized Structure Formation: Ant Trails

As our next example of non-equilibrium statistical mechanics and emergence in complex systems we will briefly consider an algorithmic model inspired by ant trail formation. The model is schematic, simplistic and its relevance to the actual mechanism involved when real ants form trails is

not known in detail. Nevertheless, the model is an interesting example of how emergent structures can appear from a dynamical algorithm.

The model describes how the path selected by ants gradually converge towards the *shortest* path between the nest and a location of food, as a result of ants' tendency to walk around at random combined with a preference for following the smell (the pheromone trail) left behind by preceding ants (Camazine et al. 2001; Solé and Goodwin 2000). The model discussed here is presented by Danilo Benzatti at <http://ai-depot.com/CollectiveIntelligence/Ant.html>; but a rich literature on individual based models of formation of patterns by social insects exists (Camazine et al. 2001; Solé and Goodwin 2000; Schweitzer et al. 1997; Bonabeau et al. 1998; Feltell et al. 2006).

We imagine a network of possible paths around the ant nest (see Fig. 3).

The nest is located at one node. Around the nest many edges connect a system of nodes. The ants can only move along the edges and in this way travel from node to node. At some of the nodes food is present. Often more than one possible route will lead from the nest to the food. How do ants, with no global overview and no sophisticated means of measuring traveled distance, identify the shortest route from the nest to a food

position? The assumption is that all what an individual ant is able to do is:

- (1) **Ant Motion:** Perform random walks.
- (2) **Effect of ant on path:** Lay down a unit of pheromone when traversing an edge.
- (3) **Feedback:** Feel attracted to pheromones deposited on the edges. The more pheromones the more an ant is attracted to an edge; and the more likely it is that the ant chooses to walk along that edge.
- (4) **Return to nest:** When food is found the ant follows its own pheromone trail back to the nest.

The reason this algorithm can converge towards the shortest path, is that the shortest path between the nest and the location of the food will have more ants traveling along its edges per time, and therefore will have a higher pheromone concentration than the longer paths.

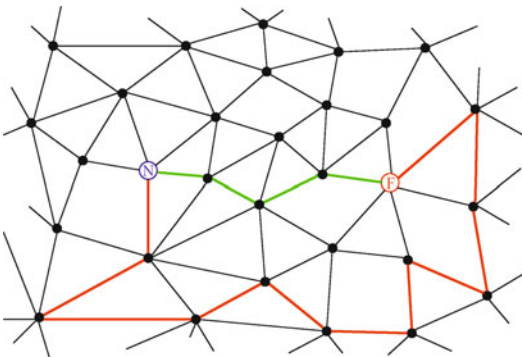
The details of the algorithm is as follows. Let the nodes be enumerated by $i = 1, 2, \dots, N$. Let edges between node number i and node number j be labeled E_{ij} . Each edge carries a time-dependent pheromone weight $\phi(E_{ij}, t)$. When an ant traverses an edge it deposits one unit of pheromone leading to

$$\begin{aligned}\phi(E_{ij}, t) &\mapsto \phi(E_{ij}, t + 1) \\ &= \phi(E_{ij}, t) + 1.\end{aligned}\quad (71)$$

At each node the ants chose probabilistically between the edges sprouting from the node. The probability $p(E_{ij}, t)$ that an ant chooses a certain edge E_{ij} among all the edges connected to a specific node number i is given by

$$p(E_{ij}, t) = \frac{\phi(E_{ij}, t)}{\sum_l \phi(E_{il}, t)}.\quad (72)$$

At the start of the simulation all ants are in the nest. Next they begin their random exploration of the network. When an ant locates the food, it picks up a unit of food and returns to the nest along the path it followed on its way out. On the return journey pheromones are also laid down,



Complex Systems and Emergent Phenomena, Fig. 3 A network of possible paths the ants can choose between as they travel from the nest at N to the food at F . The *green* short path will maintain a high level of pheromones, and will continue to attract ants, while the longer *red* path will gradually sustain a high level of pheromones and will therefore cease to attract ants

reinforcing this specific path. Finally it is assumed that the pheromones evaporate at a constant rate, say,

$$\begin{aligned}\phi(E_{ij}, t) &\mapsto \phi(E_{ij}, t + 1) \\ &= \phi(E_{ij}, t) - v\Theta(E_{ij}, t).\end{aligned}\quad (73)$$

(Note the Θ -function [defined as $\Theta(x) = 1$ for $x > 0$ and $\Theta(x) = 0$ for $x \leq 0$] ensures that the evaporation stops when there are no more pheromones on an edge, i.e. when $\phi(E_{ij}) = 0$.) Thus, paths rarely used will lose their pheromone signature and will not be attractive to the ant, whereas the pheromone level will be maintained along the more often used paths. Thus, the shorter paths with a more frequent ant-traffic will prevail over the longer paths, since the ants on the latter paths visit the individual edges less frequently.

The collective effect of this algorithm is to find the shortest path between nest and food, although the individual ant doesn't need to know that this is what is going on. For more detail see (Benzatti) and for modeling of emergent collective intelligence and pattern formation amongst social insects (see Camazine et al. 2001; Solé and Goodwin 2000; Schweitzer et al. 1997; Bonabeau et al. 1998; Feltell et al. 2006). It is still an open question how to represent algorithmic models, like the one described in this section, in a precise way.

Summary and Future Directions

We have described a specific example where one can follow in great detail the steps from one level of structure to the next in the hierarchical order of matter. Topological defects arise as coherent structures of the “atoms” at one level and can be considered as (composite) particles at the next level. Their interaction can be derived from the behavior of the constituent “atoms”. Many different systems may support composite particles that interact in the same way. We looked in particular at vortex physics, where the Kosterlitz–Thouless transition is caused by the logarithmic interaction

between the topological defects. The one most important fact in determining the KT-transition is that both energy and entropy depend logarithmically on length scale for the two-dimensional topological charges. This example is hoped to make clear that within equilibrium statistical mechanics emergent phenomena can be described and analyzed in great quantitative detail.

When we move to systems out of equilibrium, which of course by far constitute the majority, no universally applicable formalism exists so far. We illustrated, however, by two very different examples that emergent collective behavior produced by interactions between components can also in non-equilibrium situations be modeled either by use of various mathematical techniques or through the application of computer simulations.

I will finish by suggesting the following *conclusion*. There is nothing mysterious about emergent phenomena. They are a wonderful thing – but they are not of new character, something science never has seen or dealt with before. On the contrary, I will claim that understanding emergent phenomena is exactly what all science is aimed at. Often this is not so explicitly clear as in the examples discussed above where the emphasis is explicitly on the macroscopic, or systems level, effects of the interactions between the components constituting the system. Nevertheless, even when one studies, say, atomic physics (as in contrast to statistical physics), one is dealing with the effect of interacting components. An atom consists after all of interacting protons, neutrons and electrons and the properties of the atom are the emergent result of the interactions between these particles.

Notwithstanding, the focus of the statistical mechanics approach is towards generality. As illustrated by our discussion of the XY -model and the Kosterlitz–Thouless transition, the same phenomenology can be observed in many very different systems with very different types of components (magnetic moments, atoms in a lattice, superfluids etc.), if the interactions between the components possess equivalence at a mathematical level. It is this generality that leads people

to suggest that even simple model studies may sometimes be of relevance to seemingly much more complicated situations. In the future we are bound to see the statistical mechanics approach to emergent phenomena being applied to a much broader range of problems than was traditionally the case. We see attempts in fields like biology and economics, but also in linguistics, to develop pertinent statistical mechanics models. Examples include phenomena ranging from gene regulation to the social behavior of insect colonies and from stock market fluctuations to management of logistics. So far statistical mechanics has mainly been developed under the influence of physics and methods like the Renormalization Group arose. It will be very interesting to follow how statistical mechanics broadens its arsenal of tools as emergent phenomena in other fields are approached from the viewpoint of statistical mechanics.

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Polymer Physics

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Article Outline

Glossary

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Glossary

R Radius of gyration of a polymer chain

N , M Degree of polymerization or number of monomers in a polymer chain, molecular weight

ξ The screening length or correlation length in semi-dilute polymer solutions; the length over which local density is dominated by a single chain

N_e , M_e Entanglement degree of polymerization and molecular weight

l_p Persistence length of polymer chain

ν “Flory” exponent of a polymer chain relating R and N so that $R \sim N^\nu$

$S(k)$ Scattering structure factor from a polymeric fluid as function of scattering vector $k = 4\pi \sin \theta / \lambda$ where λ is the wavelength and θ the scattering angle of the experiment

$\Pi(c)$ Osmotic pressure of a solution as a function of concentration c

σ_{ij} Components of the stress tensor

d , D Dimensions of a macromolecular object and its embedding space

$R(n, t)$ Functional description of a macromolecular contour as functions of monomer number n and time t

$G(t)$ Time-dependent relaxation modulus

η Viscosity

k_B Boltzmann’s constant

χ Flory interaction parameter between monomers of different chemistry

Definition of the Subject

Physics is uniquely endowed among the sciences with complete freedom from restriction to any particular domain of the physical world. It is able to turn its particular outlook on the scientific program and its special set of experimental and theoretical tools to most material phenomena. In particular it is not limited to any particular length scale, but is sensitive to the emergence of new structures and processes of any size. So macromolecular science, born of the chemistry of the early twentieth century, soon gave rise to a branch of physics that seeks to understand the special phenomena emerging from extremely large “polymer” molecules and polymeric matter. Much of the impetus behind a physics of polymers came from the discipline’s developing theoretical tools, such as field-theory (born from quantum mechanics), and the renormalization group (born from the statistical mechanics of phase transitions), but in new guise. Polymers are giant, usually linear molecules constructed as covalently bonded chains of identical units, or monomers. Individual polymer molecules may contain hundreds or even millions of monomers. Initially disfavored by an organic chemistry community that prized exactitude, polymers were largely ignored since their molecular weight was inexact within a single sample. However, biology knew long before we did that the properties of polymers met the essential requirements of living organisms. Polymers

constitute nature's scaffolds from the macroscopic (bone, collagen) to the microscopic (filamentous actin, polymerized tubulin), her force-generators (myosin, dynein, and kinesin protein polymers), her information-processing networks (peptide-binding proteins, polysaccharides), and her instruction sets (the nucleic acid family of polymers including DNA). Much of the reason for this lies in the unique set of physical properties of polymeric matter. Some of these have now familiar application in plastic materials from packaging to high-performance fiber and even addressable polymeric electronics. Yet polymer physics is much more than the application of statistical mechanics and spectroscopy to a class of molecular matter; it has taught our discipline about some of its own deep structural connections. Path-integral techniques at the heart of theoretical polymer physics were adopted from readily developed tools in quantum field theory and magnetism. Flexible linear-like objects occur in many other avenues of the subject, superconductivity, and plasma turbulence to name two. Above all polymer physics has provided us with a classic example of emergent simplicity from bewildering complexity, so beloved of our subject. It shows every indication of providing in future an essential Ariadne's thread to guide us in our exploration of complexity itself. It will certainly underpin the urgent search for a sustainable plastics materials economy. Like the human energy budget, fossil fuel sources may serve to kick-start an advanced materials technology, but cannot sustain it.

Introduction

The fascinating physics of flexible polymers flows from both necessity and beauty. Born of the early investigations into the phenomenon of the elasticity of natural rubber (Kuhn 1936; Guth and Mark 1934), then out of the rapid growth in synthetic polymer materials in the post-war years, the need to understand and control the processing of such highly viscoelastic liquids as polymer melts, and to understand the properties of the resulting materials led rapidly to fundamental investigations led by physicists who saw an opportunity to explore

the fundamental structures of a new class of matter. Flory (1953), Zimm and Stockmayer (1949), and Edwards (1976) asked how large would macromolecules, linear or branched, be, while Zimm (1956) and Rouse (1953) asked how such giant molecules would move. Paralleling developments in solid-state many-body physics, the focus of investigations moved from single-chain to many-chain systems, which we review below in sections "Single Polymer Chain Physics" and "Equilibrium Properties of Many-Chain Fluids." These pioneers were already using a beautiful notion that was to take hold of condensed-matter physics in the mid-twentieth century – that of *universality*, or the independence of physical phenomena from local, small-scale details. The emergence of universal properties is usually associated with "critical phenomena" (Zinn-Justin 1993), since near phase transitions, the spatial scale of correlated fluctuations may hugely exceed molecular dimensions. Any properties that depend on these fluctuations (an example would be compressibility of a fluid near its critical point, and especially the *exponent* with which it vanishes as the temperature tends to its critical value) will then be insensitive to molecular detail. In field theories of both condensed and high-energy matter, the field-fluctuations "renormalize" microscopic constants into new emergent numbers on which the physics at coarser length scales (or lower energies) may be built (a famous example is the charge of the electron). Although there is at first glance no apparent neighboring critical point in the case of polymeric fluids, both universality in exponents and renormalized quantities appear in abundance. Moreover, there is a natural large number associated with mesoscopic, rather than microscopic length scales. The defining feature of a polymer is, after all, its large "degree of polymerization," N , the number of monomers linked together covalently to form the polymer chain. (The literature discusses interchangeably N and the *molecular weight* M of the chains, given in terms of the monomer molecular weight m_0 by $M = Nm_0$.) At the most basic level of inquiry into polymer structure, experiments and simulations asking how the average end-to-end distance R of a polymer molecule in solution depends on its degree of

polymerization N began to suggest a universal scaling behavior:

$$R \sim N^\nu \quad (1)$$

with an exponent ν , dependent only on the embedding dimension d and first calculated by Edwards to be $\nu = \frac{d}{d+2}$. It assumes a rather larger value in solution ($\simeq 0.59$) than the simple random walk value of 0.5 (de Gennes 1986), due to the self-exclusion of the monomers. More phenomena reminiscent of other areas of condensed matter appeared at the level of many-body effects. In the dense limit of polymer melts and concentrated solutions, where chains are highly overlapped (and in embedding dimensions greater than 4, the “upper critical dimension” of the self-exclusion problem), the exponent ν reassumes the value of 1/2 of the ideal Gaussian random walk (“Gaussian” because the ensemble of spatial end-to-end vectors of the polymer chains is normally distributed). Closer inspection revealed this to be true above a “screening length,” introduced into polymer physics by Edwards (1966). The screening length ξ itself may be directly measured by neutron scattering, and depends on concentration via another universal scaling exponent, related to ν (Adam and Delsanti 1984):

$$\xi \sim c^{\frac{\nu}{3\nu-1}}. \quad (2)$$

The picture we have built up of a many-chain polymer solution so far is summarized in Fig. 1,

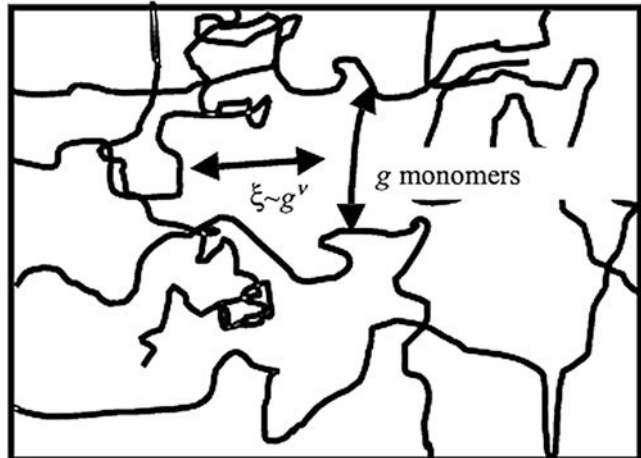
where atomic detail at the monomer level is far below the resolution of the diagram. As the polymer concentration increases, so the screening length or “mesh size” decreases. A typical strand of chain, whose end-to-end distance is ξ , dominates the monomer concentration within the volume it spans.

Both experimental and theoretical evidence of universality continued to build up. Even in the case of dynamics, the many-chain system of a polymer melt followed the ideal, local-dissipation theory of Rouse (1953) for sufficiently low molecular weight chains (see below section “Dynamics of Polymeric Fluids”) that assumed ideal Gaussian chains. It became clear that Rouse’s result can be seen as a fixed “point” of all theories of polymer dynamics in which linear connected objects are ideal and are subject to local dissipation (in dilute solution, far-field hydrodynamics destroys this locality (Zimm 1956)). For example, lattice models of polymer dynamics with local update rules renormalize to the continuum Rouse theory at large enough length scales (Verdier and Stockmayer 1962).

It seemed as though the huge connectivity of macromolecules acts to freeze-in long-range order, even though there is no true thermodynamic transition nearby. Such suspicions were confirmed by the demonstration of direct isomorphisms of the calculation of statistical mechanical partition functions of polymers, both dilute and concentrated, onto idealized spin-lattice models of

Polymer Physics,

Fig. 1 Schematic picture of universal structures of screening (overlap) length ξ and the number of monomers g that just spans ξ



magnetism (de Gennes 1986). It is indeed the high molecular connectivity, as the inverse of the degree of polymerization, N^{-1} , that plays the part of proximity to the distance from a critical point in the spin model:

$$N^{-1} \sim \varepsilon \equiv \frac{T - T_c}{T_c}. \quad (3)$$

So by exhibiting physics in which an ensemble of macromolecules of polystyrene (PS) exhibits the same emergent behavior as polyisoprene (PI) or polybutadiene (PB), following scaling laws, and tractable by application of statistical mechanical field theories (Zinn-Justin 1993), polymer physics drew together many of the strongest conceptual strands of the century.

More, however, has proved to be true in the realm of *topological* effects. The polymer melts of industrial polymer processing are very highly overlapped on the molecular level, where it becomes immediately apparent that molecular relaxation processes controlling elastic stress are prolonged to very long times indeed. All the important phenomenology is covered in Ferry's seminal survey of polymer viscoelasticity (Ferry 1986). Mechanical experiments restricted to a range of intermediate timescales of the plateau are hardly able to distinguish between the polymer melt and a rubber, in which the chains are permanently cross-linked to each other at very rare points, sufficiently for each chain to be permanently immobilized from large-scale diffusion. Conceptually, the absent "cross-links" were replaced in the minds of engineers and physicists alike by "entanglements" (Ferry 1986). These loosely defined objects were assumed to represent the topological constraint that covalently bonded molecular chains may not pass through each other. The effective distance between these objects could be calculated, employing rubber elasticity theory (see below), to deduce the degree of polymerization between entanglements N_e , or the equivalent "entanglement molecular weight," M_e . The number N_e consistently turned out to be of order 10^2 , indicating a length scale for an "entanglement spacing" of 50–100 Å, depending on the particular chemistry. This is highly significant for us, because it shows that small chains on the

threshold of feeling topological interactions are real polymers, already long enough to show to a good approximation all the universal properties of statistical connected chains. It also suggests that the role of topology in highly entangled ($N \gg N_e$) polymer fluids has the potential to be treated universally. Further evidence of universality in entanglements came from experiments in which the polymers were diluted to a volume fraction ϕ_p by a compatible solvent, indicating that $M_e \phi_p^{-\alpha}$ where the scaling exponent $\alpha \simeq 1$ (Adam and Delsanti 1984). The dependence of melt viscosity η (at fixed temperature) on molecular weight also exhibits remarkable universality over very many different polymer chemistries (Ferry 1986) closely matched by $\eta \sim M^{3.4}$, providing that the molecular weight lay well above the entanglement threshold M_e suggested by their high-frequency elastic modulus. We review this rapidly progressing area in section "Dynamics of Polymeric Fluids."

New phenomena arise when different chemistries of monomer are introduced into the same chain. Effective repulsive interactions between heterogeneous monomers create a tendency for strong spatial correlations of chemical type. In blends of more than one type of homogeneous polymer, the result is often a demixing transition with near-universal structure and dynamics (Koningsvelt et al. 2001). When the chemical species are combined into the same chain in regular "blocks" of controlled molecular weight, demixing occurs on the scale of the chains themselves, giving an extremely rich variety of spatially periodic nanoscopic structures, self-assembled micellar structures, and controlled collapsed forms. Both chain composition and temperature act as control parameters of a structural space that becomes increasingly biomimetic as the information content of the macromolecular sequence increases. Experiment and theory are reviewed in section "Multi-Phase Polymeric Fluids."

Single Polymer Chain Physics

It should not be surprising that the notion of complexity should arise even in the context of the

“single particle” domain of polymer physics: that of a single molecule. For already a macromolecule contains many degrees of freedom that are coupled in nonlinear ways. Not only this but also at the single-chain level emergent co-operative properties arise. We briefly survey three important cases of single-chain physics: the non-interacting chain, the effect of excluded volume, and the role of charge.

Ideal Non-interacting Chains

The first and most fundamental of these underlies the physics of rubber elasticity: it is the emergence of an entropic Hookean spring for macrostates of a single polymer chain in thermal equilibrium defined in terms of its end-to-end vector $\mathbf{R}$. We recap briefly here the statistical physics of a polymer chain, modeled as a *random walk* in space and subject to some local rule for spatial links. An example is the freely jointed chain, in which the orientations of a set of linked rods are uncorrelated. The step length of the chain corresponds to the Kuhn length, b , of the polymer (the shortest independently oriented segment length). It is not as small as a monomer length, but usually four or five monomers long.

For polymer statistics suppose a whole walk has N links. Let the end-to-end displacement of an individual chain be $\mathbf{R}(N)$. From the theory of random walks: $\langle R^2(N) \rangle = Nb^2$ and the probability density for the end-to-end vector $G(\mathbf{R})$ must have Gaussian form (from the law of large numbers, since each vector step is an independent random variable whose sum is $\mathbf{R}(N)$). So,

$$G(\mathbf{R}, N) = \left(\frac{3}{2\pi Nb^2} \right)^{3/2} e^{-3R^2/2Nb^2}. \quad (4)$$

The macrostate of an ensemble of such chains is defined by the chain end-to-end vector $\mathbf{R}$. The microstates are the different specific paths through space that have $\mathbf{R}$ as their end-to-end displacement. Each individual path, or microstate of the chain, will be specified if the spatial position of each link is known. We will use the notation $\mathbf{R}(n)$ for the position of the n^{th} link. The full time-dependence of the chain would then be described by the function $\mathbf{R}(n, t)$, extended to the two dependent variables of

contour position n and time t . The role of Brownian motion can be cast in the form of Langevin equations for $\mathbf{R}(n, t)$ (see Rouse model, section “Dynamics of Polymeric Fluids”), but here we exploit it as a generator of ergodic exploration of all chain configurations in the ensemble. The number of configurations with fixed end to end vector $\mathbf{R}$ is just the corresponding fraction of total microstates $\Omega(\mathbf{R}) = \Omega_{\text{TOT}} P(\mathbf{R})$. Since the entropy of the walk $S = k_B \ln \Omega(\mathbf{R})$ we have $S(\mathbf{R}) = \text{const.} - \frac{3k_B R^2}{2Nb^2}$. The conformational free energy of the chain $F(\mathbf{R}) = U - TS$ has $U = 0$ since there are no sources of internal energy. This yields for the free energy of a chain of fixed end-to-end vector $F(\mathbf{R}) = \frac{3k_B T R^2}{2Nb^2}$. Finally we may derive the thermodynamic force (or “Brownian tension”) on the chain end-to-end vector as

$$f = -\nabla F(\mathbf{R}) = -\frac{3k_B T}{Nb^2} \mathbf{R} \quad (5)$$

and recognize a linear elastic spring law. That is, a random walking polymer at finite T is a Hookean spring with spring constant $\propto T/N$.

The analogies between the statistical mechanics of random walks and the quantum mechanics of spinless particles also emerge from this analysis. Applying Eq. (4) to small subchains of path length ΔN allows the (careful) taking of a limit so that

$$G(\mathbf{R}, \Delta N) = \left(\frac{3}{2\pi \Delta N b^2} \right)^{3/2} e^{-\frac{3}{2b^2} \left(\frac{\partial \mathbf{R}}{\partial N} \right)^2 \Delta N}.$$

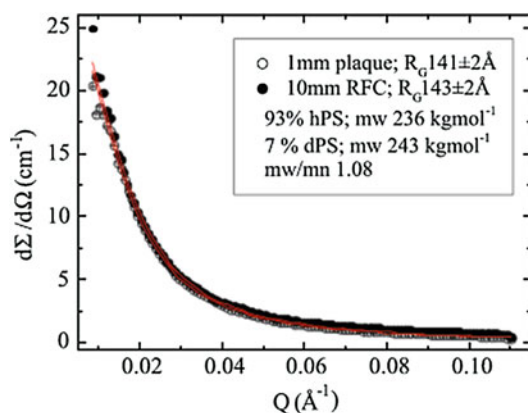
The notation G for the probability distribution is suggestive: this descriptor of the chain has the structure of a propagator. The complete end-to-end propagation of (4) can be written as the sum over all possible intermediate positions of the meeting points of all smaller subchains, which in turn is just an example of a Feynman path integral over all possible paths of the polymer contour $\mathbf{R}(n)$:

$$G(\mathbf{R}, N) = \int_{\mathbf{R}(0)=0}^{\mathbf{R}(N)=\mathbf{R}} e^{-\frac{3}{2b^2} \int_0^N \left(\frac{\partial \mathbf{R}}{\partial n} \right)^2 dn} D[\mathbf{R}(n)]. \quad (6)$$

The propagator structure arises because the properties of the chain at equilibrium are

governed by its partition function, which in turn is a sum over microstates that are in this case just the possible paths of the chain. An analogous integral arises in Feynman's form of quantum mechanics because the sum over all trajectories that gives the (complex) amplitude for particle propagation is just the same geometrical set of paths. The difference is that in polymer statistical mechanics the phase angle attributed to the path is imaginary, giving a real argument of the exponential in the path integral. A rich set of techniques flow naturally from this analogy: since the propagator also obeys Schrödinger's equation, the equilibrium configuration of ideal chains in confined geometries and external potentials can be solved by any technique developed for the quantum mechanical case (de Gennes 1986).

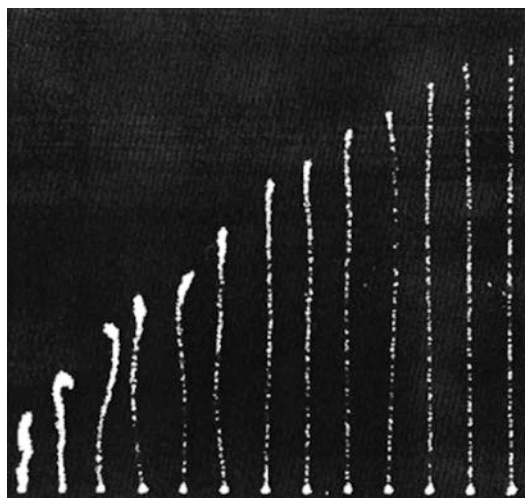
Experiments on single chains have until recently been indirect ensemble measurements. However, neutron-scattering can give averaged single chain properties because of the very different scattering lengths of hydrogen and deuterium nuclei. It is relatively straightforward to replace chemically some or all of the hydrogen atoms in a fraction of the chains in a polymeric fluid. When the chains themselves are monodisperse, the small-angle scattering pattern is identical to that of the population of labeled chains. Figure 2 shows an example of scattering from a 7% labeled fraction of polystyrene chains with a narrow distribution of molecular



Polymer Physics, Fig. 2 Small angle neutron scattering (SANS) data averaged over angles for a monodisperse polystyrene melt. The theoretical curve is that calculated from a Gaussian propagator

weight. Early experiments of this type showed the remarkable result illustrated here that the single chains in a densely packed melt actually assume an ideal (effectively non-self-interacting) set of configurations described by the Gaussian propagator of Eq. (4) (see section “Equilibrium Properties of Many-Chain Fluids” below). Much more recently the advent of recombinant DNA, fluorescent labeling, and video confocal microscopy has begun to make direct inspection of individual polymer molecules possible in restricted circumstances. Even very high molecular weight DNA has a random-walk molecular dimension $bN^{1/2}$ below the resolution limit of optics, but if the chain is stretched out much larger dimensions are accessible approaching bN , so that some of the predictions of single-chain elasticity can be explored.

Figure 3 shows one famous example that actually illustrates chain response as the maximum elongation is approached. In this limit the Gaussian approximation breaks down badly and a divergence of force with extension is measured. The form of the divergence is, unlike the linear entropy-dominated range of elasticity, not universal among local polymer chemistries, but depends on the form of the local structure and its response to tension. Another analogy with high-energy physics



Polymer Physics, Fig. 3 Images of a 64μ long DNA molecule held in place at one end by optical tweezers and stretched out by hydrodynamic flow of increasing velocity from left to right. Reprinted with permission from (Perkins et al. 1995)

arises here: *strong* applied forces measure structure at *smaller* length scales. This is powerfully illustrated by the high-force asymptote of two models of flexible polymers, the freely jointed chain (FJC) and the worm-like chain (WLC). The first models the local structure of a chain as N freely hinged but infinitely stiff rods each of length b . Such a chain has a maximum extension of its own contour length $L_0 = Nb$, but at low forces responds with the linear behavior of the Gaussian chain so that the force f with extension L follows $f \sim k_B T (L/Nb^2)$. The force diverges as $L \rightarrow L_0$ with the asymptotic form $f(L) \sim (1 - L/L_0)^{-1}$. The WLC introduces a finite bending rigidity everywhere along the chain so that the internal energy of a configuration $\mathbf{R}(n)$ can be written as

$$E = k_B T l_p \int_{n=0}^N \left(\frac{\partial \mathbf{R}(n)}{\partial n} \right)^2 dn \quad (7)$$

with the constraint that $\left| \frac{\partial \mathbf{R}(n)}{\partial n} \right| = 1$. The stiffness is written as $k_B T l_p$ in terms of the “persistence length” l_p because at equilibrium the chain is locally stiff at smaller length scales and flexible over longer lengths. This statement can be made exact by considering the correlation function of the orientation of the chain:

$$\left\langle \frac{\partial \mathbf{R}(n_1)}{\partial n} \frac{\partial \mathbf{R}(n_2)}{\partial n} \right\rangle = e^{-|n_1 - n_2|/l_p}.$$

Although this model also shares the Gaussian linear response of the FJC, it possesses quite different asymptotics at high force (Marko and Siggia 1995), following $f(L) \sim (1 - L/L_0)^{-1/2}$. The calculation takes the response under the force of all harmonic normal modes of the Hamiltonian (7), the more gentle divergence arising from the successive suppression of contortions of the chain at smaller and smaller wavelength as the force increases.

Self-Interacting Chains: Excluded Volume

As pointed out in the introduction, real polymer chains in solution are not typically Gaussian. The reason is that the path integral of (6) overcounts the allowable configurations of the chains,

including those that cross themselves. The modification to the Hamiltonian that achieves the monomeric self-exclusion with maximum simplicity and generality is the “Edwards Hamiltonian” (Edwards 1965):

$$G(\mathbf{R}, N) = \int_{\mathbf{R}(0)=0}^{\mathbf{R}(N)=\mathbf{R}} e^{-\frac{3}{2b^2} \int_0^N \left(\frac{\partial \mathbf{R}}{\partial n} \right)^2 dn - w \int_0^N \int_0^N \delta[\mathbf{R}(n) - \mathbf{R}(n')] dn dn'} D[\mathbf{R}(n)].$$

Although formally the delta-function potential removes only a volume of phase space of zero measure from the path integral, its anticipated use within field-theoretic tools for the solution of the model mean that it represents a renormalized local repulsion between monomers of the chain at the level of this universal coarse-grained theory. From this starting point one can proceed by several methods: self-consistent field treatment of the excluded volume term (Edwards 1965), mapping onto problems in critical phenomena (de Gennes 1972), direct renormalization-group calculation (des Cloiseaux 1981), and Monte Carlo numerical enumeration (Mazur and McCrackin 1968). For a comprehensive and technical review see des Cloiseaux and Jannink (1990). The essential structure within the self-consistent field methods is the same as that of an early calculation by Flory (Flory 1953) who balanced the scaling forms of the free-energy contributions from chain elasticity (R^2/N) and excluded volume (N^2/R^d) in d -dimensional space and minimized to give the dependence of the scaling exponent for chain size v as

$$v = \frac{d}{d+2}. \quad (8)$$

This is fortuitously accurate in all dimensions from $d = 1$ (where it is exact) to $d = 4$, which it correctly identifies as the upper critical dimension of the problem since the Gaussian exponent of $v = 1/2$ is recovered here. However, the method is unreliable for the calculation of other quantities because in dimensions less than four the excluded volume term is not perturbative for any strength of the parameter w in the large- N limit. This really forces a renormalization approach to the problem, already achieved in the case of spin interactions in

magnets at the ferromagnetic critical point. A formal and beautiful exact mapping first pointed out by de Gennes exists between the excluded volume chain and an analytic continuation of the Heisenberg model in which the number of spin components goes to zero (de Gennes 1972). The analogy arises because the calculation of the correlation function between the magnetic spins on any two sites of the lattice in the magnet model can be written as a weighted sum over all non-intersecting paths that connect the two sites within the lattice. So formally,

$$\langle S_i S_j \rangle = \sum_N \Omega(N) e^{-\epsilon N}, \quad (9)$$

where $\Omega(N)$ counts the number of self-excluding walks of length N connecting the sites and ϵ measures the dimensionless temperature difference from the ferromagnetic critical point as in Eq. (3). The analogy led directly to the first calculated values for the Flory Exponent ν using diagrammatic expansion methods developed originally from Feynman's perturbation tools for quantum electrodynamics. In three dimensions the problem is non-perturbative – the exponent departs from the mean-field value for all values of the excluded volume parameter w no matter how small, providing that the chains are long enough. The calculation of ν requires first taking the problem in four dimensions, where it becomes perturbative, then taking a double expansion in w and in the analytic continuation of dimension below 4. For short enough segments on the other hand, the chains do not depart strongly from ideal behavior. There is a characteristic length scale at which the energy of self-exclusion equals the thermal energy kT below which statistics are near-ideal and beyond which the chains are swollen. Subchains of this intermediate length scale are known as “thermal blobs.” In $d = 3$ the value of $\nu \simeq 0.588$, in close agreement with the value predicted (fortuitously) by (8).

The behavior of chains under an attractive two-body interaction constitutes an emergent phenomenon that mirrors that under repulsion discussed above. The experimental case is that of a “poor solvent” where monomers of the polymer now enjoy a favorable interaction. Now the chains are densely packed for high enough molecular

weights so that $\nu = 1/d$ above the thermal blob size. In the limit of infinite molecular weight the transition from a swollen to collapsed chain becomes thermodynamic. This is possible to realize experimentally in some cases by simply controlling the solvent quality though control of temperature. There exists in these cases a critical point known as the “theta temperature” at which the effective two-body monomer-monomer interactions from excluded volume and solvent-induced attraction exactly cancel, leaving only three-body and higher terms. The “coil-collapse” transition is not sharp (only becoming so in the thermodynamic limit of infinitely long chains).

The collapsed and swollen chain configurations of real chains leave their traces on the emergent elastic properties of single chains that we examined above in the ideal case. For example, now the effective Hookean spring force-distance relation $f(R)$ is modified to $f \sim R^{\frac{1}{1-\nu}}$ in general.

The Role of Electrostatic Charge

A recently very active area in polymer physics that has produced a number of surprises is the form of emergent behavior arising from the combination of electrostatic charge, polymeric connectivity, and counter-charges in solution. This is the case of “polyelectrolytes” – polymers containing charged monomers. Complex emergent behavior is perhaps unsurprising since all three have the propensity to generate long-ranged interactions that are candidates for generators of qualitatively different physics from the local interactions examined in the last section.

The static configurations of a polyelectrolyte are radically different from those of a neutral flexible chain in solution. Constructing a mean-field “Flory” type theory for a chain containing a fraction f of monomers carrying charge e that, balancing electrostatic energy with configurational entropy, yields the result (Rubinstein and Colby 2003):

$$R \simeq N b f^{2/3} \left(\frac{l_B}{b} \right)^{1/2} \quad (10)$$

showing that at this level the chains will be completely stretched at the scaling level. This result contains one of the several new length

scales that appear in complex fluid electrostatics, the Bjerrum length:

$$l_B \equiv e^2/(\epsilon kT).$$

This is the distance between charges at which the electrostatic and thermal energies are comparable.

Charged configurations of this extreme kind are not realized globally, since counterions are universally present to ensure overall neutrality. Their presence in solution screens the “bare” long-range electrostatic repulsion beyond the “Debye screening length”:

$$l_D \equiv \left(\frac{\epsilon kT}{n_0 e^2} \right)^{1/2}.$$

This is not the length scale on which the charged chains adopt random-walk configurations; however, since there is typically a strong repulsion (many kT) between chain segments adjacent by l_D , providing the charge fraction is great enough. The emergent persistence length is another new scale:

$$l_p = l_D \left(\frac{l_D l_B}{b^2} \right) f^2.$$

A different set of structures arises if the energy competition is between electrostatic repulsion and chain-collapse in a poor solvent. Without electrostatics the chain will collapse into a compact globular form with $v = 1/d$ to minimize the total contact between monomers and solvent, restricting it to the surface of the globule. The surface energy rises as γR^2 , but is eventually overcome by the electrostatic self-repulsion from the globule’s charge, which rises (in three dimensions) as $N^2 f^2 e^2 / R \sim R^5$. This instability was identified as a cause of droplet breakup in simple fluids by Lord Rayleigh. The free-energy minimum is achieved in the polymeric case by a configuration resembling a string of pearls, in which the polyelectrolyte breaks up into small globules that closely balance the surface and electrostatic energies, connected by stretched strands of chain. It is a rare example of heterogeneous configurations

minimizing the free energy at the level of a single chain (Dobrynin and Rubinstein 2005).

The combination of persistent, or rod-like, configurations and counter-charges leads to other remarkable properties of charged polymers. The entropy of confinement of counterions within a cylindrical region around an extended polymer of radius R decreases as $kT \log R$ per ion. In this geometry this has the same functional form as the electrostatic attraction (providing that R is less than the screening length), which depends on the charge per unit length of the polymer ρ as $(\rho e/\epsilon) \log R$. Providing $(\rho e/\epsilon) > kT$, most of the counterions in solution balancing the charge on the polymer will be closely bound to it, the phenomenon of “Manning condensation” (Manning 1969). This criterion is equivalent to evaluating the number of counterions per Bjerrum length. If this is less than one, then all counterions are effectively free; otherwise there is significant condensation onto the chain.

The charge clouds condensed in the vicinity of neighboring polymers sustain thermal fluctuations that correlate via the long-range electrostatic interaction in an analogous way to the electronic origin of the Van der Waals interaction. Providing the fluctuations are large enough (these are enhanced by ions of high valency), then the fluctuation-induced attraction between the counterion clouds may actually overcome the electrostatic repulsion of the bare polyelectrolyte charge. For polymers in solution like charges may indeed attract! This effect is responsible for the attraction and bundling of polymers of DNA, which carries a strong negative charge (Ha and Liu Andrea 1998).

Equilibrium Properties of Many-Chain Fluids

We have seen that the thermodynamic properties of single polymer chains exhibit both richness and a high degree of universality. Both aspects of the emergent properties of polymer physics extend to many-chain systems in which the molecular chains become strongly overlapped. When this happens the quality of the solvent (controlled with temperature) that for single chains gave rise to the coil-collapse transition, swollen statistics, and the pseudo-ideal theta temperature, now

control co-operative phenomena such as the emergence of an osmotic pressure, and phase separation.

Semi-dilute Solutions

The existence of the coil-size itself $R \sim N^\nu$ sets a new concentration regime, termed “semi-dilute,” that only exists in the case of polymeric fluids. We have already encountered it, and its key attributes, in the introductory discussion of Fig. 1. The semi-dilute concentration range covers those cases where the chains themselves are strongly overlapped but where the volume fraction taken up by monomer rather than solvent molecules is still small. The structure of the solution when the polymer-solvent interaction is favorable is entirely dominated in this regime by the new length scale of the screening length ξ . The physics of this length scale is readily detected in two ways: by direct structural probes such as neutron scattering, and by the solution property of osmotic pressure. If scattering contrast exists between monomer and solvent, then the scattering intensity and scattering wavevector k measures the fluctuations in monomer concentration within volumes of fluid of size k^{-1} . For large length scales $k \ll \xi^{-1}$, there are no correlations between one element bounded by a screening length and its neighbors: the identity of a single chain is lost at these scales where it is highly overlapped with others. At the other limit, all scattering for $k \gg \xi^{-1}$ is governed by correlations along single chain segments within such correlation volumes, and the scattering is identical to that from a single chain. Since chains have a spatial scaling structure whether in theta or good solvents, power-law behavior is induced in the scattering as well. The physics is captured by a generalization of the Ornstein-Zernicke scattering function:

$$S(k) \simeq \frac{S(0)}{1 + (k\xi)^{1/\nu}} \quad (11)$$

illustrated in the figure (Daoud et al. 1975). The exponent ν is the same as that determining coil size for single chains discussed in the previous section.

The osmotic pressure as a function of monomer concentration $\Pi(c)$ of a semi-dilute polymer solution is also connected with the structure of closely packed correlation volumes that emerges from the screening-length picture. This is because Π measures the change of free energy with concentration, itself dominated by the balance of chain entropy and chain contact-energy. Since all sub-chain configurations within each correlation volume ξ^3 are sampled ergodically, but all correlations at greater length scales lost, the consequence is that the free-energy density carries the structure of kT/ξ^3 , or one thermal degree of freedom per correlation volume. Since the concentration of the correlation length is calculable in terms, once more, of the Flory exponent ν , from Eq. (2), the concentration dependence of the osmotic pressure follows $\Pi(c) \sim c^{3\nu/(3\nu-1)}$ in the semi-dilute regime. The same result can be arrived at by anticipating a scaling structure that crosses over to the correct ideal-gas form under truly dilute conditions, writing

$$\Pi(c) = \frac{kT}{b^3} \frac{c}{N} f\left(\frac{c}{c^*}\right). \quad (12)$$

Here $f(x)$ is a scaling function that tends to unity for small argument, and to a power law $f(x) \sim x^z$ for largest. The concentration c^* is the overlap threshold separating dilute and semi-dilute regimes, where individual coils just begin to overlap. Insisting that for $c \gg c^*$ the osmotic pressure should not depend on chain length N (this is equivalent to the loss of correlations beyond ξ) fixes the power $z = \frac{1}{3\nu-1}$ and the result $\Pi(c) \sim c^{3\nu/(3\nu-1)}$ is recovered. Experiments at different molecular weights and chemistries in good solvents collapse well onto the scaling form of (12) (Noda et al. 1981). A formal route to the calculation of the solution properties of correlation, free energy, and osmotic pressure was discovered by Des Cloiseaux as a generalization of the magnetic spin-analogy of de Gennes. A diagrammatic expansion of n -body chain interactions is performed for the zero-spin limit of the model, but this time in the presence of an external field. This acts as a fugacity for chains, and creates a system where renormalization group methods

may be used, again in expansion around four spatial dimensions, to calculate exponents such as z (des Cloiseaux and Jannink 1990).

The semi-dilute structure for polyelectrolytes (see above) is complex. In the absence of added salt, small-angle scattering experiments display a peak, rather than the “shoulder” of the Ornstein-Zernike-like structure function of uncharged chains, indicating a dominant correlation length which is not entirely understood. The scaling of the peak position k_m with concentration c , $k_m \sim c^\delta$ varies as the chains become overlapped, with the exponent δ changing from $1/3$ to $1/2$ in the semi-dilute regime, and finally to $1/4$ in concentrated polyelectrolyte solutions. These regimes have also appeared in approximate field-theoretic calculations (Muthukumar 2016).

Complex Topology Polymers and Gelation

The emergent properties of polymers in solution, it should be clear by now, arise from the connectivity of chains, either on its own or in the presence of other physical interactions such as excluded volume or electrostatics. It is also the essentially topological properties of connectivity that endow polymer physics with its universality. It is therefore of interest to explore the consequences of altering the chain topology in more complex ways. One very practical way of doing this is to introduce cross-links chemically into a polymer solution (industrially this is the route to preparation of rubbers). In the limit of high cross-link density the result is a system of chains that have a significant number of their degrees of freedom “quenched” (chemically connected monomers on different chains are perpetually forced into proximity). That the resulting physical object is a solid when the original system was fluid is by no means an obvious result, and emerges only delicately from the treatment of the statistical mechanics of quenched disorder. Historically, methods originally developed to treat the model systems of “spin-glasses” were the first to treat the cross-linked polymeric fluid from this point of view, among them the “replica method” of Edwards (Deam and Edwards 1976). Here the formal free energy of the rubber as an average over the logarithms of quenched partition

functions with different configurations of cross-links $\{N_x\}$:

$$F(N, N_x, \Lambda) = kT \langle \ln Z(N, \{N_x\}, \Lambda) \rangle_{\{N_x\}}$$

is treated using the formal limit $\log Z = \lim_{n \rightarrow 0} \left(\frac{Z^n - 1}{n} \right)$. This amounts to the statistical mechanics of an unquenched ensemble of replicas of the original network, but in the limit (analytically continued) of the number of replicas tending to zero. The liquid-solid transition emerges as the physical consequence of a mathematical symmetry-breaking between the replicas in the evaluation of the free energy, and a shear modulus grows as the third power of the difference between the cross-link density and a critical value for the onset of the solid (Castillo and Goldbart 2000).

Although the formal treatment of rubber elasticity is very subtle, there are good approximations that have generated a sequence of semi-empirical models capable of capturing not only stress generation in cross-linked rubbers but also the temporary stress generated in entangled polymeric fluids (see below). These begin with identifying a length scale at which the deformation Λ is imposed on chain segments affinely, and below which the chains are assumed to be able to explore all microstates. Applying the result for the effective elasticity of the chain segments (5) above yields an expression for the bulk stress tensor in terms of the average configuration of the subchains:

$$\sigma_{ij} = \frac{3k_B T}{b^2} \mathbb{C} \left\langle \frac{\partial R_i}{\partial n} \frac{\partial R_j}{\partial n} \right\rangle. \quad (13)$$

These results obtain for the case in which the cross-links are suddenly imposed upon an equilibrium semi-dilute or concentrated polymer solution. If they are introduced gradually, a richer structure arises in which chains of increasingly branched nature are created well before the critical liquid-solid transition. If this process is imposed mathematically on an ensemble of ideal chains, an ensemble of very compact branched polymers results with a Flory exponent of $\nu = 1/4$.

From the definition of ν , (1), we see that its inverse $1/\nu \equiv D$ plays the role of a dimension. Ideal linear chains are in this sense two-dimensional objects, but ideal branched polymers are four-dimensional! This does not present a necessary difficulty at fixed spatial scales, since the individual molecules of finite molecular weight are very sparse, but at high enough molecular weight there will not be sufficient space in three embedding dimensions to contain such objects without overlap. This must occur in successive cross-linking, because calculations of the distribution of molecular weights that result from random insertion of cross-links (this may be done elegantly by the use of generating functions (de Gennes 1986)) give a result of the form:

$$P(M) = M^{-\tau} f(M/M_x), \quad (14)$$

where τ is a “Fisher exponent” and $f(x)$ a cut-off function that limits the distribution function to a highest molecular weight of M_x . This upper molecular weight itself diverges as another scaling function of the difference in cross-link density from the critical value $M_x \sim |p - p_c|^{-1/\sigma}$. This class of critical phenomena generated by topological connectivity is called “percolation” and generates beautiful physical effects in polymers. Like other critical phenomena associated with thermodynamic phase transitions it possesses universality classes in which the values of the exponents are independent of the geometry of local interactions. We can see that the mean-field (ideal) value of $D = 4$ (and $\tau = 5/2$) is not sustainable in three-dimensional space: the branched polymers must swell by excluded volume so that they do not overlap strongly with themselves (or with subclusters of larger molecules) (Cates 1985). Applying this requirement on the non-overlap of clusters of all molecular weights generates a relationship between the exponents τ , D , and the embedding dimension d called the hyperscaling relation:

$$\frac{d}{D} = \tau - 1. \quad (15)$$

This holds for a wide range of “bare” fractal dimensions D since the excluded volume drives

systems to marginal overlap at all length scales stably: if the overlap reduces for larger chains, then they suffer less excluded volume and swell less, consequently increasing overlap once more. The values for percolation in three-dimensional space are $D \cong 2.53$ and $\tau \cong 2.18$. Should the overlap increase, then the consequent increased self-repulsion increases swelling with the opposite effect. The structure implied by (15) is self-similar on a grand scale: not only are the individual molecules self-similar but the ensemble also satisfies self-similarity at all length scales in the marginal overlap of clusters of all sizes. There is no correlation length and the scattering function is a power law.

A major new class of complex polymeric materials exploits a class of chemical exchange reactions that endow a thermally controlled rate of partner-exchange to the cross-links in a gel. Termed “vitrimers” because of their fine temperature control of processing (akin to that of silica glass), they constitute a new class of temporary cross-linked materials (Denissen et al. 2015). The sudden loss of elasticity that would arise from a simple switch from permanent cross-links to those of finite lifetime (and so a temperature-dependent density of active cross-links), and an approach to the percolation threshold discussed above, is replaced by a dynamical evolution of network topology that maintains the concentration of cross-links fixed. Such materials also possess “self-healing” properties: as long as fractures can be supported through breakage of the temporary bonds only, mechanical fissures and faults in vitrimers will heal over the same timescale as the cross-link reorganization.

Dynamics of Polymeric Fluids

Complex, emergent phenomena extend from static structure of polymeric fluids into their rich dynamic properties. This is especially true of the semi-dilute and concentrated cases when interactions between distinct chains are very strong and the conformational dynamics highly

coupled. But even in the case of dilute or effectively uncoupled dynamics the scaling structures we saw in equilibrium pattern the behavior out of equilibrium. The experimental tools deployed also mirror those used for statics: direct structural probes of light or neutron scattering possess dynamic counterparts in photon correlation spectroscopy (Jian et al. 1996) and neutron spin-echo (Higgins and Benoit 1994). Specific averages over bond correlation dynamics are available from dielectric spectroscopy (Watanabe 1999) or NMR relaxation (Klein et al. 1998). Emergent effects at the level of the fluid are most striking in their rheology (McLeish 2002). At the level of linear response, the rubber-elastic stress generated by small deformations decays with a function $G(t)$ characteristic of the molecular structures present: the phenomenon of viscoelasticity. In strongly nonlinear flows other effects appear, such as the effective decrease in viscosity with shear rate, complex transient behavior in stress response, and the generation of rich stress fields and non-inertial elastic instabilities in nontrivial flows. We first review briefly the dynamic properties of single polymer chains before treating more extensively the complex dynamics of entangled systems.

Single Chain Dynamics

In the simplest fundamental model of polymer dynamics, due to Rouse, we make three key simplifying assumptions (Rouse 1953). Their physical validity depends on the effectiveness of screening (Edwards 1966) of both static and hydrodynamic quantities in a melt. In the case of concentrated solutions, screening will not be operative at length scales below the mesh size ξ , but will hold at larger scales. But these contain the length scales of entanglement effects, so in the solution case also, coarse-grained local dynamics are expected to follow the Rouse model locally. Even in concentrated polymeric fluids the dynamics of chains (and subchains) below a characteristic molecular weight are not strongly coupled to the presence of other chains. The central assumptions are:

- Gaussian Chains: in which the force on a subchain segment n is the net entropic force from its neighbors. In the continuum representation we have adopted, this is equivalent to a thermodynamic force at each point of the chain of $-\frac{\partial}{\partial n}(\kappa \frac{\partial \mathbf{R}}{\partial n}) = -\kappa \frac{\partial^2 \mathbf{R}}{\partial n^2}$ with $\kappa = \frac{3k_B T}{b^2}$.
- Local drag: the drag force on a subchain segment comes from frictional drag against background without long-range hydrodynamic effects of backflow (this works in melts where all long-range mediated backflows are screened). This force is $\zeta \frac{\partial \mathbf{R}}{\partial t}$ with ζ a drag coefficient per segment.
- Brownian motion: a random force $\mathbf{f}(n, t)$ acts on each subchain with correlation times much faster than any polymer dynamics to be modeled by the theory.

The monomeric drag constant ζ_0 will parametrize all our theoretical models, setting the timescale for both Rouse and, subsequently, entangled, motion. The balance of entropic, drag, and random forces on the chain of N subchains is the Rouse equation:

$$\zeta_0 \frac{\partial \mathbf{R}}{\partial t} = \frac{3k_B T}{b^2} \frac{\partial^2 \mathbf{R}}{\partial n^2} + \mathbf{f}(n, t). \quad (16)$$

The noise on each subchain is related to its frictional drag by the generalized Einstein relation as above:

$$\langle \mathbf{f}(n, t) \mathbf{f}(m, t') \rangle = 2\zeta_0 k_B T \mathbf{I} \delta(n - m) \delta(t - t'). \quad (17)$$

The Rouse dynamical Eq. (16) is diagonalized by the transformation:

$$\mathbf{R}(n, t) = \mathbf{X}_0(t) + 2 \sum_{p=1}^{\infty} \mathbf{X}_p(t) \cos\left(\frac{p\pi n}{N}\right). \quad (18)$$

The $\mathbf{X}_p(t)$ are the time-dependent amplitudes of the “Rouse modes” of the polymer chain. These are just the (vector amplitude) Fourier modes of the chain path $\mathbf{R}(n, t)$ with respect to the arclength

coordinate n . The key result for us is the time correlation function of the mode amplitudes, which is:

$$\langle X_p(t) X_q(t') \rangle = \mathbf{I} \frac{k_B T}{k_p} \delta_{pq} e^{-|t-t'|/\tau_p} \quad (19)$$

with $k_p = \frac{6k_B T p^2 \pi^2}{N b^2}$.

Each mode has its own relaxation time $\tau_p = \zeta/k_p$ that decrease rapidly (as $1/p^2$) with mode index p . The longest of these relaxation times $\tau_1 = \frac{\zeta N^2 b^2}{3\pi^2 k_B T}$ has special significance. It is known as the *Rouse Time*, and often given the notation τ_R . It is the time for relaxation of the overall shape of the molecule (it is the relaxation time of the amplitude of the normal mode with fewest nodal points, $\cos \frac{\pi n}{N}$), and is also the time for a Gaussian Rouse chain to diffuse its own radius of gyration.

What does the local motion of this model chain look like? We expect for short intervals that the chain contour may have adjusted locally, but retain a very similar global configuration (see Fig. 4). In order to answer this question, and to compare with local diffusion probes of NSE and NMR on unentangled dynamics, we need to calculate the correlation function $\phi_n(t) \equiv \langle (\mathbf{R}(n, t) - \mathbf{R}(n, 0))^2 \rangle$ that describes the mean displacement over time of monomers on the chain. Summing over the independent normal modes gives:



Polymer Physics, Fig. 4 A Rouse chain changes its configuration (from solid to dashed curve) locally but not globally in times shorter than τ_R

$$\phi_n(t) = 6D_{CM}t + \frac{Nb^2}{3\pi^2} \left(\frac{t}{\tau_R} \right)^{1/2} \alpha.$$

Here $\alpha = \frac{1}{2} \int_0^\infty z^{-3/2} (1 - e^{-z}) dz \simeq 1.77$ is a purely numerical constant. The result is remarkable: each monomer executes an “anomalous” or sub-Fickian diffusion, such that its mean square displacement goes as $t^{1/2}$ rather than t (as for ordinary diffusion). This behavior persists until times longer than the Rouse time, after which each monomer is carried by the (faster) center of mass motion of the whole molecule. This anomalous diffusion is simply a consequence of chain connectivity: the further a monomer travels under Brownian motion, the greater is the length of chain that must be correlated with it and the greater the effective drag over that length scale.

The (deviatoric) stress formula

$$\sigma_{ij} = \frac{3k_B T}{b^2} \mathbb{C} \left\langle \frac{\partial R_i}{\partial n} \frac{\partial R_j}{\partial n} \right\rangle$$

we derived above Eq. (13) leads, via representation in terms of the Rouse modes (Doi and Edwards 1986), to an expression for the time-dependent modulus function following a step strain $G(t) = \sigma_{xy}(t)/\gamma$. Each mode decays back to equilibrium anisotropy with its own characteristic time. The power-law distribution of modes then gives:

$$G(t) = \frac{\mathbb{C} k_B T}{N} \sum_p e^{-2p^2 t / \tau_R} \quad (20)$$

$$\approx \mathbb{C} k_B T \left(\frac{t}{\tau_1} \right)^{-1/2} e^{-t/\tau_R}.$$

So we find that, until a final crossover to an exponential decay beyond the Rouse time, the Rouse model has a relaxation modulus which is a power-law of $G(t) \sim t^{-1/2}$. Note that the longest relaxation time scales with molecular weight as N^2 , but the viscosity scales as $\mathbb{C} k_B T N$. This is because at the longest relaxation time that sets the value of the viscosity, the stress is carried only by the lowest Rouse mode; the density of these modes is just one per chain, or $\frac{\mathbb{C}}{N}$.

Beautiful generalizations of such dynamical scaling behavior arise in the case of marginally overlapped fractal clusters, such as those arising from gelation transitions. Long-range hydrodynamic interactions are effectively screened, but entanglement effects are negligible. So now the Rouse Eq. (16) generalizes to solving the eigenvalues of the Laplacian (right-hand side of (16)) on a fractal cluster with high degree of branching. Locally (for high-frequency modes) this is indistinguishable from the case of linear chains, but at longer wavelengths than the chain length between branch points, the effective dimensionality of the cluster rises. Just as in many cases it is possible to represent the mass distribution with an effective dimensional exponent $D = 1/\nu$, so the Laplacian eigenfunctions of a self-similar branched object possess a “spectral dimension” d_s and the density of states in k -space can be written

$$g(k) dk \cong k^{d_s-1} dk. \quad (21)$$

The combination of the scaling dimension of individual clusters and the self-similarity of the molecular weight distribution via the Fisher exponent yields a generalized power-law for stress relaxation (Cates 1985). For Rouse dynamics (local friction) and hyperscaling the result depends only on the fractal dimension of the clusters

$$G(t) \simeq \frac{kT}{b^3} \left(\frac{t}{\tau_0} \right)^{-\frac{3}{D+2}}. \quad (22)$$

The value of the dynamic exponent z in $G(t) \sim t^{-z}$ for three-dimensional percolation is therefore predicted to be $z \cong 0.66$. Experiments on critical gels of unentangled chains confirm this (Lusignea et al. 1995).

Polymer Dynamics with Hydrodynamics

When macromolecular chains are not strongly overlapped, the effects of hydrodynamic flow within the solvent makes a strong difference to the absolute timescales of subchain motion, and to the scaling form of diffusive, sub-diffusive, and orientational relaxation (Doi and Edwards 1986).

The reason for this is the long-range nature of the flow-field in a Newtonian fluid in the appropriate non-inertial (“Stokes”) limit applicable to polymer solutions. The central hydrodynamic result needed to develop a fully hydrodynamic theory of polymeric fluids can be captured as the velocity perturbation $\mathbf{v}(\mathbf{r})$ resulting from a point force $\mathbf{f}$ applied at the point $\mathbf{r} = \mathbf{0}$ within such a fluid:

$$\mathbf{v}(\mathbf{r}) = \frac{1}{6\pi\eta r} \left(\mathbf{I} - \frac{\mathbf{r} \mathbf{r}}{r^2} \right) \cdot \mathbf{f} \quad (22a)$$

The distance-dependent tensor operating on the force is the “Oseen tensor,” and scales like an electrostatic potential with $1/r$, but with additional structure that preserves the fixed density of the fluid under the perturbed flow (technically ensuring that it is divergence-free). That this “backflow” is all-important in the case of polymers can be understood by a simple scaling estimation of the total effect on the velocity at any monomer on a chain from the rest of the chain. For if the chain is a Gaussian random walk, the average density of monomers from the same chain at a distance r from any one of them falls off as $1/r$. The contribution to the backflow from these monomers also falls off as $1/r$ from the Oseen result, but the number of such sources of flow perturbation increases with the area of the shell at a distance r (r^2). So each shell contributes equivalently and the velocity “perturbation” from all monomers diverges until cut-off by the entire chain, or be a distance over which the sign and size of the perturbing force fails to correlate. It is instructive to note that for extended rods, rather than polymer coils, this same argument leads to the weak, logarithmic, divergence of hydrodynamic corrections to local friction in that case.

The consequences of this hydrodynamic argument are remarkable: (1) a polymer coil will essentially drag all its internal solvent with it as it diffuses; (2) the “Rouse modes” of the internal dynamics of chains are still approximately good dynamical modes for the hydrodynamic case.

Entangled Polymer Dynamics

Richer behavior still emerges in the realm of interchain *topological* effects that dominate in

fluids where chain overlap is very strong. The polymer melts of industrial polymer processing are very highly overlapped on the molecular level, where it becomes immediately apparent that molecular relaxation processes controlling elastic stress are prolonged to very long times indeed. The classic “relaxation modulus” $G(t)$ measuring stress linear response to a step strain records a “plateau” value before a terminal relaxation time that increases rapidly with molecular weight, in strong contrast to the power-law decays discussed above. Experiments restricted to the timescales of the plateau are hardly able to distinguish between the polymer melt and a rubber, in which the chains are permanently cross-linked to each other at very rare points, sufficiently for each chain to be permanently immobilized from large-scale diffusion. Conceptually, the absent “cross-links” were replaced in the minds of engineers and physicists alike by “entanglements” (Ferry 1986). These loosely defined objects were assumed to represent the topological constraint that covalently bonded molecular chains may not pass through each other. The effective distance between these objects could be calculated, employing rubber elasticity theory,

$$G_N^{(0)} = k_G \frac{RT\rho}{M_e}$$

(with the constant $k_G = 1$ for “affine” and $1/2$ for “junction fluctuation” models of elasticity) to deduce the degree of polymerization between entanglements N_e , or the equivalent “entanglement molecular weight,” M_e . The number N_e consistently turned out to be of order 10^2 , indicating a length scale for an “entanglement spacing” of 50–100 Å, depending on the particular chemistry. This is highly significant for us, because it shows that small chains on the threshold of feeling topological interactions are real polymers, already long enough to show to a good approximation all the universal properties of statistical connected chains. It also suggests that the role of topology in highly entangled ($N \gg N_e$) polymer fluids has the potential to be treated universally. Further evidence of universality in entanglements came from experiments in which the polymers were

diluted to a volume fraction ϕ_p by a compatible solvent. The apparent entanglement molecular weight $M_e \sim \phi_p^{-\alpha}$ where the scaling exponent $\alpha \simeq 1$ (Adam and Delsanti 1984).

Other experiments had pointed to the existence of a topological feature at this coarse-grained scale of structure. Careful measurements on rubbers of controlled synthesis had shown that the shear modulus was higher for a network of long chains than a model incorporating cross-links alone would predict (Treloar 1975). Other “trapped entanglements” on the same scale as the melt value of N_e seemed to contribute to the elasticity. Advanced theories of rubber elasticity have been able to treat rubber networks in terms of the two distinct constraints of physical cross-links and trapped entanglements (Ball et al. 1981; Rubinstein and Panyukov 2002). A remarkable universality also emerged in measurements of the scaling of melt viscosity η on the molecular weight M of very many different polymer chemistries (Ferry 1986):

$$\begin{aligned} \eta &\sim M^1 & M < M_e \\ \eta &\sim M^{3.4} & M > M_e. \end{aligned} \quad (23)$$

For each material, a critical molecular weight, M_e emerged, above which the viscosity rises very steeply with molecular weight. Furthermore, within experimental error, this explicitly dynamical observation was linked phenomenologically to the essentially static measurements of the plateau modulus by the correlation

$$M_e \simeq 2M_e. \quad (24)$$

This connection between essentially dynamic (M_e) and static (M_e) experiments, observed over a wide range of chemistries, is strong evidence that topological interactions dominate both the molecular dynamics and the viscoelasticity at the 10 nm scale in polymer melts (and at correspondingly larger scales for concentrated solutions).

Without going beyond rheological measurements on bulk samples, there has long been other very strong evidence that molecular topology is the dominant physics in melt dynamics. This emerges from the phenomenology of “long

chain branched” (LCB) melts. These materials, commonly used in industry, possess identical molecular structure to their linear cousins on the local scale, but contain rare molecular branches (they differ from the “polymeric fractals” discussed above in that their linear sections are long enough to be entangled). The density of branching varies from one branched carbon in every 10,000 to 1 in 1000. This level is chemically all but undetectable, yet the melt rheology is changed out of all recognition if the molecular weight is high enough (Small 1975). Providing that $M \gg M_e$, the limiting low-shear viscosity may be much higher for the same molecular weight. Moreover in strong extensional flows the melt responds with a much higher apparent viscosity than in linear response. This phenomenon, vital for the stable processing properties of branched melts, is called “extension hardening.” The effect is all the more remarkable because in shear flows, branched, as well as linear, melts exhibit a lower stress than would be predicted by a continuation of their linear response (Meissner 1975) (they are “shear-thinning”). A fascinating example of the difference between linear and branched entangled melts is well-known from flow visualization experiments. The velocity field in a strong “contraction flow” of a linear

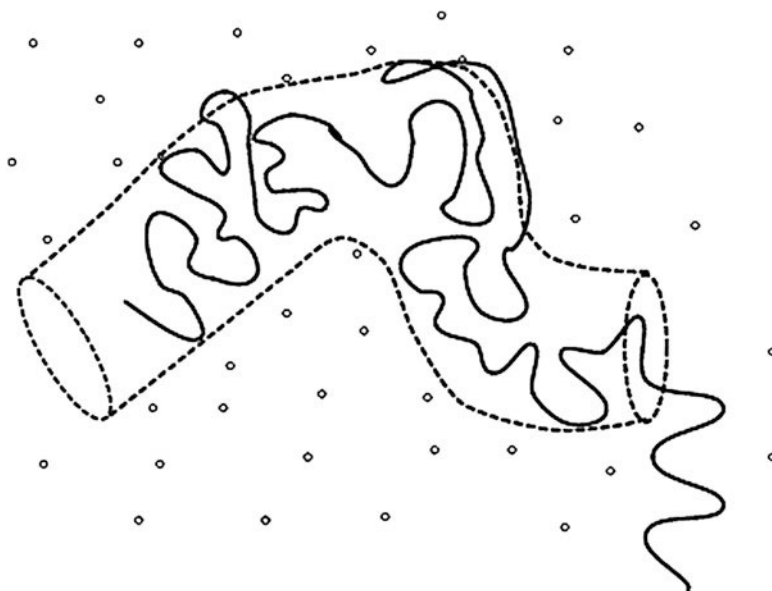
polymer melt resembles that of a Newtonian fluid, while that of a branched polymer sets up large vortices situated in the corners of the flow field. Slight changes to the topology of the molecules themselves give rise to qualitatively different features in the macroscopic fluid response.

The most successful accounts of these phenomena have been given by the *tube model*. The idea is to deploy the theoretical physicists’ favorite strategy of replacing a difficult many-body problem with a tractable single-body problem in an effective field. In this case the “single body” is the single polymer chain, and the effective field becomes a tubelike region of constraint along the contour of the chain. The tube is invoked to represent the sum of all topological non-crossing constraints active with neighboring chains, and the tube radius, a , is of the order of the end-to-end length of a chain of molecular weight M_e . In this way, only chains of higher molecular weight than M_e are strongly affected by the topological constraints (see Fig. 5).

The tube was first invoked by Edwards (Edwards 1967) in an early model for the trapped entanglements in a rubber network. The consequences of the idea for dynamics were first explored by de Gennes (1971), again in the context of networks. A free chain in a network would

Polymer Physics,

Fig. 5 A tubelike region of constraint arises around any selected polymer chain in a melt due to the topological constraints of other chains (small circles) in its neighborhood (diagram courtesy of R. Blackwell)

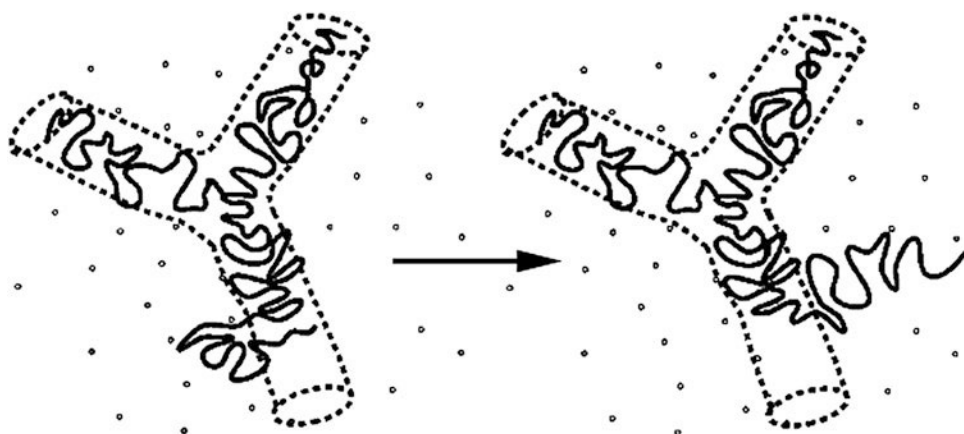


be trapped by neighboring chains into tube of radius a defined by its own contour, suppressing motion perpendicular to the tube's local axis beyond a distance of a , but permitting both local curvilinear chain motions and center-of-mass diffusion along the tube. de Gennes coined the term "reptation" for this snake-like wriggling of the chain under Brownian motion. The theory gives immediately a characteristic timescale for disengagement from the tube by curvilinear center-of-mass diffusion. This disengagement time τ_d is naturally proportional to the cube of the molecular weight of the trapped chain (this arises from combining the Fickian law of diffusive displacement of length L with time τ , $\tau \sim L^2$, recognizing that path length $L \sim M$, with one extra power arising from the proportionality of the total drag on molecular weight). Very significantly, de Gennes also realized that a tubelike confining field would endow a dangling arm, fixed to the network at one end, or belonging to a star-shaped polymer in a network, with exponentially slow relaxations. In this topology reptation would be suppressed by the immobile branch point (de Gennes 1975), and only exponentially rare retractions of the dangling arm would disengage it from its original tube (see Fig. 6 below). In the late 1970s, S.F. Edwards and M. Doi developed the tube concept into a theory of entangled melt dynamics and rheology for monodisperse, linear chains (Doi and Edwards

1986), finding extensions to flow instabilities (McLeish and Ball 1986), blends (Watanabe and Kotaka 1984), and polymers of controlled architecture that go beyond the star topology (Pearson and Halfand 1984) to H-polymers (McLeish et al. 1999) and combs (Inkson et al. 2006).

Fully atomistic simulations of polymer melts are now able to examine entanglement effects. It is now possible to conduct molecular dynamics simulations of, for example, elastically connected Lennard-Jones polymers that contain 50 chains each of 10,000 monomers well into the regime in which entanglements dominate the dynamics (Pütz et al. 2000). This technology is now at the point at which direct comparisons to experimental results such as NSE is now possible. The other advantage of large simulations is that they may mimic the "ideal" experiment in which everything may in principle be measured. This has been exploited in tests of fundamental theories of entanglements (see below) (Everaers 1998).

The growing quantity of data on branched molecules of controlled molecular weight and topology has provided severe tests of the tube concept at a level beyond that probed by linear chains (McLeish 2002). The hierarchical nature of configurational relaxation at the molecular level in particular has been turned from speculation into orthodoxy. In the simplest case of entangled star polymers, the theory suggests that chains escape



Polymer Physics, Fig. 6 The process of arm retraction predicted by the tube model for the case of dangling entangled arms, as from the branch point of a star polymer.

Unlike in reptation, reconfiguration of the outer parts of the arm occurs many times for one relaxation of deeper segments

from their confining tubes not by reptation, which is suppressed by virtue of the immobile branch point, but by a process of *arm retraction*, present but largely eclipsed in the case of linear polymers (see Fig. 6).

The effect on the viscosity of replacing linear molecules with those of identical molecular weight, but of star topology, is striking: now

$$\eta \sim e^{\alpha(M_a/M_c)} \quad M_a > M_c \quad (25)$$

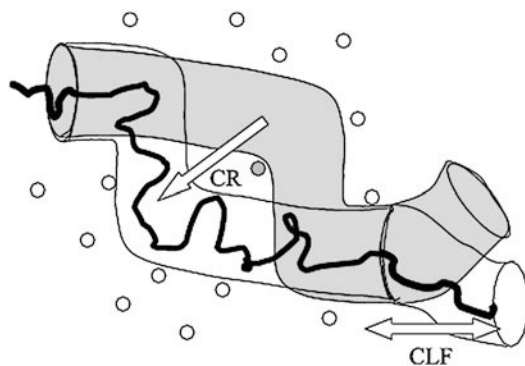
is the dominant form of the molecular weight dependence (where M_a is the molecular weight of the dangling *arm*), rather than $\eta \sim M^{3.4}$ (in the case of linear polymers the entire effect of these fluctuations is to change the apparent exponent of this relation from 3 to 3.4 up to a high molecular weight of order 10^3 entanglements, where it saturates at the “bare reptation” value of 3). In entangled melts with repeated levels of branching, the retraction dynamics of outer levels generate the slower retraction of inner branches in a hierarchical way. The most advanced application of this process has been on materials that combine the complexity of the gelation-point critical ensemble (see section. “[Single Chain Dynamics](#)” above) with the physics of entanglement. The broad rheological spectrum of branching chemistry that builds molecules by grafting back repeatedly previously synthesized molecules (Das et al. 2006a) is captured by these calculations. When the percolation transition is approached by cross-linking entangled polymers, there exists a measurable region in which mean-field statistics ($D = 4$) actually hold. Stress relaxation from such an ensemble is logarithmic in this regime, but is closely modeled by a dynamical scaling form in which the dynamic exponent z is small (being inversely proportional to the number of entanglements between branch points) (Das et al. 2006b).

The wealth of experimental and simulation data has sharpened the theoretical picture. Without exploding with new parameters, it has been possible to capture, in a single model, modes of entangled motion beyond pure reptation. In linear response *contour length fluctuation* (CLF), the Brownian fluctuation of the length of the entanglement path through the melt, modifies early-

time relaxation. Similarly the process of *constraint release* (CR), by which the reptation of surrounding chains endows the tube constraints on a probe chain with finite lifetimes, contributes to the conformational relaxation of chains at longer times. Both the processes of CLF and CR contribute to the quantitative understanding of linear rheology, such that the $\eta \sim M^{3.4}$ law is no longer a mystery (Milner and McLeish 1998; Likhtman and McLeish 2002), but much of the newer data still need to be examined quantitatively as sensitive tests of the detailed physics, and many puzzles remain. These two additional processes are visualized in Fig. 7.

Nonlinear Flow of Polymeric Fluids

In strong deformations the additional processes of *chain stretch*, *chain retraction*, and *branch-point withdrawal* emerge on the level of single chains (the latter exclusively in the branched case), and *convective constraint release* (CCR) at the level of co-operative motion (Marrucci and Non-Newton 1996; Mead et al. 1998; Likhtman et al. 2000). The most advanced formulation of the tube model for linear polymers keeps the coarse grained



Polymer Physics, Fig. 7 A cartoon of the processes of contour length fluctuation (CLF) and constraint release (CR) on a linear polymer in a constraining tube. In CLF the chain end retracts via longitudinal fluctuations of the entangled chain, but without requiring center-of-mass (reptation) motion. Re-extension of the chain end may explore new topological constraints, reconfiguring the tube. In CR, an entanglement with a neighboring chain (shown hatched) may disappear, allowing effective conformational relaxation of that part of the tube, again without reptation of the test chain itself. In both cases the former tube configuration is shown *dark*, the new, *light*.

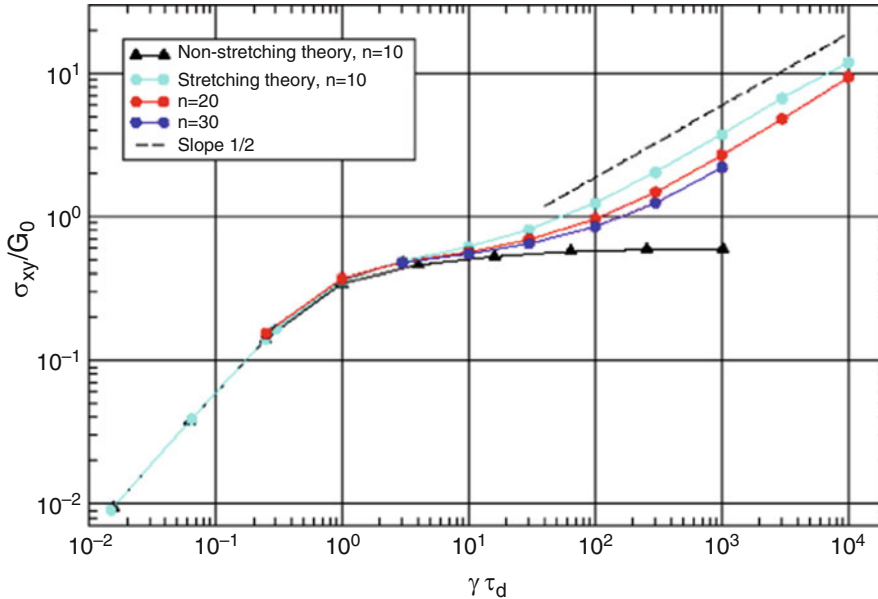
coordinates of the chain, and allowing CCR events to generate local Rouse jumps of the tube (Likhtman et al. 2000). The idea is to retain full information about average chain trajectories instead of working indirectly with dynamic equations for the stress and orientation tensor. This approach also allows quantitative predictions about the single chain scattering function $S(q)$, and to develop a *local* description of CCR events. The main assumptions of the first version of the theory (valid when there is no chain stretch) are: (i) that CCR operates locally in reorienting chain segments both into and away from the flow direction, and (ii) that neither the number of entanglements per chain $Z = M/M_e$ nor the tube diameter a changes. The first assumption endows the tube itself with a Rouse-like motion in which the local hopping rate is coupled to the global deformation rate via a single new parameter. The second (constant length) assumption introduces a difference from ordinary Rouse-chain motion, and limits the range of validity at first (but see below) to $0 < \dot{\gamma} < 1/(\tau_e Z^2)$.

No single set of variables will be able to diagonalize the essential entangled modes of motion, namely (i) chain reptation, (ii) chain retraction,

(iii) tube-length fluctuation and the new mode, and (iv) Rouse-tube motion. However, the theory is conventionally cast in a real-space notation for the tube trajectory $\mathbf{R}(s, t)$ and its tangent curve $\mathbf{R}' \equiv \frac{\partial \mathbf{R}}{\partial s}$, functions of curvilinear distance s from along the tube and time t . Our chains are monodisperse containing Z entanglements of tube diameter a . The (stochastic) equation of motion becomes (Graham et al. 2003):

$$\begin{aligned} \mathbf{R}(s, t + \Delta t) = & \kappa \mathbf{R} \Delta t + \mathbf{R}(s + \Delta \xi(t), t) \\ & + \Delta t \left(\frac{3\nu}{2} \frac{\partial^2 \mathbf{R}}{\partial s^2} + \mathbf{g}(s, t) \right) \\ & + \Delta t \lambda \left(\frac{Z}{2} - s \right) \frac{\partial \mathbf{R}}{\partial s} + 3D_e Z \frac{(\mathbf{R}'' \mathbf{R}')}{|\mathbf{R}'|^2} \mathbf{R}'. \end{aligned} \quad (26)$$

The terms of this formulation describe, in order, affine convection of the tube, reptation, CR Rouse motion of the tube, retraction of the chain within the tube and chain stretch. This model predicts in shear flow a near plateau of $\sigma_{xy}(\dot{\gamma})$ between $\dot{\gamma} \tau_d$ and $\dot{\gamma} \tau_R$, and an increase proportional to $\dot{\gamma}^{1/2}$ beyond that (so that the “shear-dependent viscosity” $\eta(\dot{\gamma}) \dot{\gamma}^{-1/2}$) (see Fig. 8). Both this feature and a prediction of strong



Polymer Physics, Fig. 8 Predictions of the local CCR model with chain stretch using $c_v = 0.1$ for values of $Z = 10, 20, 30$. A comparison to the non-stretching version is given

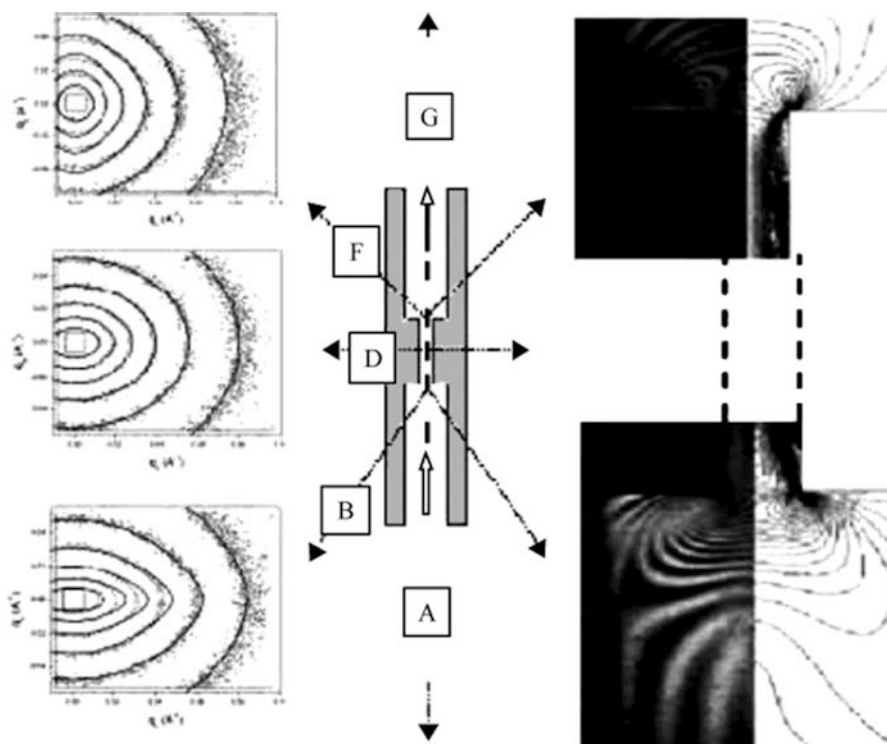
extension hardening at rates faster than the inverse chain stretch time have been quantitatively matched to experiment.

The strongest tests of the predictions for chain conformations have been performed in “neutron flow mapping” experiments (Bent et al. 2003; Graham 2006). Here a partially deuterated (for neutron scattering contrast) polymer melt of monodisperse or controlled architecture is passed continuously through a complex flow field such as a contraction, bounded by windows transparent to both laser illumination and thermal neutrons. The stress field is measured in optical birefringence, while single chain conformations are reported by the neutron small angle scattering. Scanning the apparatus across the neutron beam allows the experiment to probe regions of the flow with varying strain histories. The experiments are compared to calculations in which the model of (26) is used both to calculate the flow field itself, then the

scattering function of chains subjected to the stream lines that flow through the neutron beams.

Figure 9 shows the results of one such experiment. The key result is that relaxation to equilibrium structure takes place in the flow at timescales that depend on the chain length scale examined. It also shows that no model containing just one viscoelastic relaxation time is even qualitatively able to account for the nonlinear physics of entangled melts. The simplest must possess at least two relaxation times, corresponding to chain stretch (fast – by Rouse motion) and chain orientation (slow – by reptation). At the purely phenomenological level of the stress tensor the emergent property is a rapidly relaxing trace, and a slower traceless part to the stress.

One of the most remarkable predictions in nonlinear response of the tube model for entangled polymers addresses the fruitful system of “bimodal blends.” These controlled-composition melts

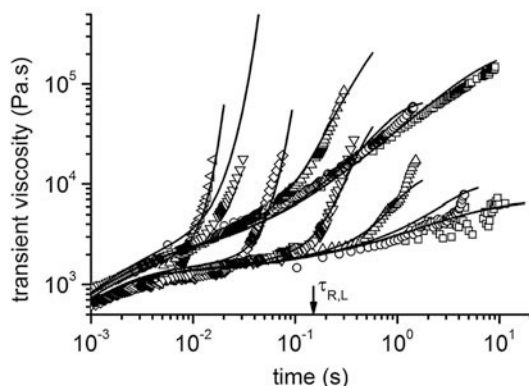


Polymer Physics, Fig. 9 A monodisperse linear entangled melt in a neutron flow mapping experiment. Flow is from bottom to top. Single chain scattering functions from windows B, D, and F are compared with contour

predictions on the left. Chain configurations relax during passage through the channel from an initial strain. On the right, contours of principal stress (left) are compared with calculations (right)

comprise two monodisperse fractions (short and long chains) of different degrees of entanglement Z_S , Z_L and a chosen volume fraction of the long chain fraction ϕ_L . The parameters range, therefore, over a three-dimensional space, even for this simple system. The linear response is already very rich (Viovy et al. 1991). It is possible, for example, for the reptation of the long fraction to be determined by a tube of entanglements formed from all the chains in the melt. However, if the difference in degree of entanglement is great enough, the constraint-release from the more rapid reptation of the short chains reveals a “fat tube,” constituted only from entanglements between long chains. In this case the terminal relaxation time is determined by a renormalized reptation of long chains within these “fat tubes.”

An even more remarkable phenomenon was predicted, then demonstrated, in strong extensional flows of such bimodal blends (Read et al. 2012). For when the constraint-release of short chains is dominant, the nonlinear stretch-relaxation (effective Rouse) time τ_{RL} for the long chains is actually *increased* by the presence of the short-chain diluent, so that $\tau_{RL}(\phi_L) = \tau_{RL}(0)/\phi_L$. The effect can be seen clearly in the comparison of the two sets of curves in Fig. 10, where the onset of



Polymer Physics, Fig. 10 (From ref. Read et al. 2012) Transient extensional viscosity for a polyisoprene bimodal blend of $Z_L = 100$, $Z_S = 7$, and $\phi_L = 0.2$ (upper curves) at rates in s^{-1} of 0.1, 1.24, 9.91, 101.6 and the same blend with $\phi_L = 0.04$ (lower curves) at rates in s^{-1} of 0.1, 0.5, 2, 9.81, 46.7, 224. Also shown are the corresponding theoretical predictions. All data and rates are time-temperature shifted to a reference temperature of 25 °C. The Rouse time of the long chains is indicated on the time axis

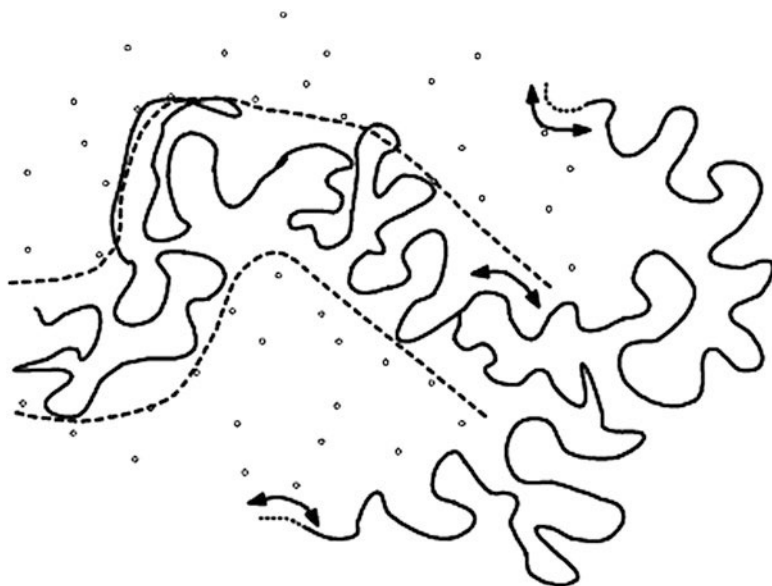
extension-hardening appears at proportionally lower flow rates for the blend with the lower concentration of long chains. The highly counterintuitive increase of stretch relaxation time when a more rapidly relaxing fraction is added arises from the subtle way that constraint-release from short chains give rise to a slower tube-length fluctuation time (in the “fat tube”), and through this renormalized process generating a corresponding stretch relaxation time in nonlinear response. The connection between extension hardening and “melt-strength” in polymer processing means that, long before this process was understood, it had been employed to stabilize processing in industrial blends. Although these are generically much more complex than the idealized bimodal blend, the high molecular weight tail of an industrially polydisperse blend may behave in the same way as the long-chain fraction of the ideal blend.

At a more approximate level, it is possible to combine the complexities of nonlinear response and complex branched topologies in entangled melts. All the linear and nonlinear molecular processes of chains in tube-like entanglement fields are present, together with one additional process, that of “branch point withdrawal.” When a strand connecting two branch points is very highly stretched, the finite size of the clusters it connects (in contrast to the network case) becomes apparent, and one of the clusters may topologically collapse into the deforming tube of the central strand. In the simplest case of the H-polymer the two outer arms are drawn into the tube of the “cross-bar” segment (see Fig. 11).

There are consequences of the process for both chain conformation (scattering) and stress response (rheology). If the retracting arms are labeled in a scattering experiment, very strong signal enhancement is seen in the direction of the deformation (McLeish et al. 1999; Heinrich et al. 2004). At the same time, the growing extensional stress, until that point resembling that of a cross-linked network, reaches a near plateau. The effect of this at the level of the process engineering is to endow strongly branched melts with both extension hardening (leading to flow stabilization) and good processability. A useful modeling tool for branched melts has been derived from the ideal

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Fig. 11 The process of branch point withdrawal: a segment with greater than equilibrium tension pulls attached dangling arms some distance into its own tube, thus shortening their effective entangled path length



“pom-pom” architecture (McLeish and Larson 1998). This generalization of the H-polymer allows the number of arms attached at either end of the cross-bar, q , to vary. So q becomes a molecular parameter controlling the degree of strain hardening. Creating multiple modes from this model allows accurate models to be built for commercial, highly branched melts (Inkson et al. 1999; Blackwell et al. 2000; Graham et al. 2001). Computing in complex geometries with these models has successfully predicted features of the flows particular to branched melts, such as recirculating vortices upstream of a contraction and very persistent sheets of high birefringence downstream from re-entrant corners, sometimes known as “stress-fangs” (Lee et al. 2001).

Multiphase Polymeric Fluids

In the foregoing, the spatial structure of polymeric fluids has remained essentially homogeneous, all heterogeneities remaining at the level of entanglements, or correlation volumes, in solution. The hidden reason for this is that we have considered systems containing just one chemistry of monomer. Yet one of the great attractions of polymers is their tendency to develop complex spatial structures when different chemistries are combined,

either in the case of entire chains, when we create *polymer blends*, or within single chains, referred to as *copolymers*. In the latter case, especially interesting structures arise when the distinct monomers are correlated in sequence along the chain, forming *block copolymers*. The simplest example would be a string of n monomers of chemistry A followed by m of chemistry B . This is an A - B diblock copolymer. The essential reason for the sensitivity to local chemistry is that the entropy of spatial translation per monomer in a polymeric fluid is extremely low. The usual Van’t-Hoff term $S_{\text{trans}} = -k T \log \phi$ is divided by the degree of polymerization of the chain so that it effectively competes with the mild Van der Waals dominated enthalpic interaction between monomer units, which tend to favor proximity of identical chemical units: polymers tend therefore toward demixing. In blends the demixing competes with the slow, viscoelastic dynamics we discussed in the last section, creating spatially complex morphologies that are determined kinetically. In the case of block copolymers, the demixing occurs locally, confined to spatial scales of the block subchain radii. The demixing now competes with the chain elasticity we discussed in section “Single Polymer Chain Physics.” The connection of polymer sequence with emergent structure illustrates the high potential information

content of a macromolecule. It is an example of the genotype-phenotype pattern developed to a much higher degree in the case of the DNA-embedded genetic code. This field, like that of controlled architecture dynamics, is an area of polymer physics where the complex emergent phenomena have required a parallel implementation of careful synthetic chemistry (Ruokolainen et al. 2005), experimental physics (Adhikari and Michler 2004), and advanced theoretical techniques (Matsen 2005) to explore, and is growing extremely rapidly.

Polymer Blends

The starting point for a conceptual understanding of the physics of polymer blends is a mean-field model for the free energy of mixing of two species such that one occupies a total volume fraction ϕ . Known as the Flory-Huggins free-energy (Koningsvelt et al. 2001), it balances the entropy of mixing of the two components against the energy difference of mixed and demixed states:

$$\Delta F_{\text{mix}} = k_B T \left[\frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln (1-\phi) + \chi \phi (1-\phi) \right]. \quad (27)$$

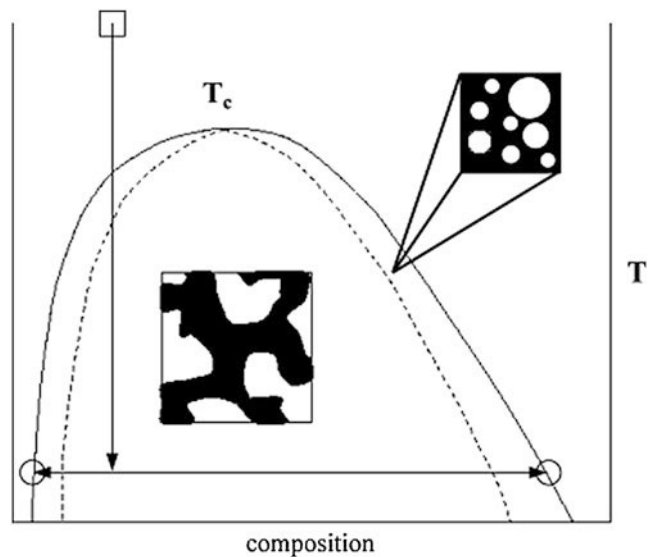
The control parameters for this theory are the two molecular weights and the (temperature

dependent) interaction (“Flory”) parameter χ . The whole system is therefore three-dimensional: the monomer interaction is best normalized with the mean molecular weight so that $\chi \bar{N}$ is the essential parameter that controls interaction strength. Then N_A/N_B becomes the asymmetry parameter while ϕ controls the composition. The possibility of phase separation means that ΔF_{mix} can be minimized by forming regions with different values of ϕ if the curvature $\partial^2 \Delta F_{\text{mix}} / \partial \phi^2$ is anywhere less than zero. This in turn occurs for all $\chi > \chi_c$. Phase separation then occurs for all systems whose mean composition falls between the two minima of $\Delta F_{\text{mix}}(\phi)$, a region that broadens as χ moves further (as temperature is changed) from χ_c .

This behavior is mapped in Fig. 12. The region between the two curves (binodal and spinodal) of the plot corresponds to compositions and temperatures where the curvature of $\Delta F_{\text{mix}}(\phi)$ is positive, producing a fluid that is *locally* stable to composition fluctuations though globally unstable to phase separation. In this case droplets of the separated phase have to nucleate, giving an initially disconnected morphology. Within the spinodal curve on the other hand, the fluid is unstable to local and infinitesimal changes in composition, so that natural thermal fluctuations of composition are amplified. The presence of a fastest growing wavelength leads to a connected (or “spinodal”) morphology.

Polymer Physics,

Fig. 12 Regions of phase separation in polymer blends with the Flory-Huggins model. Phase separation occurs within the binodal curve (solid curve), but is unstable locally only within the spinodal (dashed curve)

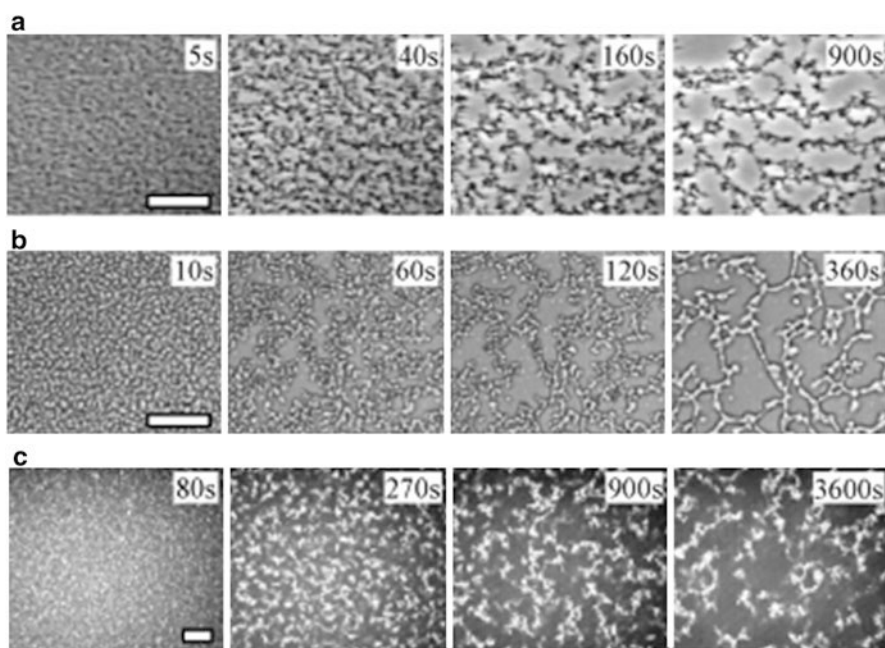


morphology for most of this region. Since the final minimum in free-energy is total phase separation, whatever intermediate structure evolves eventually coarsens with time with well-known growth laws depending on whether hydrodynamics or diffusion is dominating (Onuki 2002). This beguilingly simple map hides a great deal of latent complexity, however. More recently, the recognition that the spinodal process leads to a morphology dependent on both the local free energy and the distribution of initial fluctuations has generated experimental and theoretical explorations of the wider control space that includes trajectories across the composition diagram (Henderson and Clarke 2004), variations on boundary conditions and viscoelastic effects (Tanaka et al. 2005). A striking example is given by the “target” structures that result from kinetic trajectories that spend some time in the nucleation region of the composition space before (cooling) into the spinodal region. During the first period, small nuclei are allowed to form but sustain limited growth. Instead, the growth occurs in the locally unstable region using the nuclei as sources of unstable fluctuations. Because the Fourier wavelet

decomposition of a spherical nucleus with a sharp boundary consists of spherical waves centered on the nucleus, it is these that are amplified by the growth process, or reverse diffusion, and structures of nested spheres of varying composition appear during it. Since phase separating polymers typically also have a glass transition temperature, it is possible to quench the composition structure at any point in the phase separation.

Viscoelasticity may play a modifying role at both early and late stages of the phase separation. At early times, any dominant viscoelastic mode, such as reptation, can undergo mode-mixing with the dominant phase separation time to produce to two timescale process of separation (Clarke et al. 1997). This may result in non-monotonic concentration growth with time, since of the two resulting modes one typically decays while the other grows. At later stages, a strong viscoelasticity in at least one phase causes the heterogeneous fluid to retain the mutual connectivity of both phases for much longer than in Newtonian fluids (Tanaka et al. 2005).

Figure 13 illustrates the high degree of universality of this effect, contrasting dilute, and concentrated polymer solutions with a protein



Polymer Physics, Fig. 13 Confocal imaging of viscoelastic phase separation from (Tanaka et al. 2005) showing the time development of structure from (a) dilute polymer solution, (b) protein solution, (c) concentrated polymer solution

solution in which the protein molecules behave more as colloidal particles than polymer chains. Although the structures coarsen, they retain connectivity of the minority phase rather than suffer it breaking into droplets. A similar effect is generated by the natural composition dependence of mobility. It is unlikely that the mobilities of the two demixing species will remain independent of the local composition, since the natural drag constants within the two final demixed phases will typically differ. The phase of lower mobility then becomes kinetically quenched earlier than that of higher mobility. This nonlinearity affects the connectivity of the morphology at long times (Mao et al. 2001).

Block Copolymers

The demixing tendencies of polymers of different chemistries become very rich when it competes with the feature at the heart of polymer physics itself: that of connectivity. By connecting a chain of A -monomers to one of B -monomers, they are forced by the spatial correlations that chain connectivity induces into proximity. Within a mean field picture, the repulsive interaction in the free energy density $k_B T \chi \phi_A \phi_B$ (from the last term in (27)) competes with the entropic chain elasticity $F_{\text{elas}} = k_B T (R_A^2/N_A b^2 + R_B^2/N_B b^2)$. In contrast to previous sections, we consider first the case of dense chains (melts), then solutions, and finally the effects within single chains of such controlled chemical architecture.

Consider first the case of the *diblock* copolymer just outlined. In a melt, when the interaction parameter χ is large enough, the chains must locally segregate into regions rich in one or other of the polymers. The molecules themselves clearly minimize their contribution by situating their midpoints where the two chemistries join at the interface between the two regions. Topology dictates that at most two A -chains may span an A -rich region, so consequently the length scale of the morphology must be of the same order as the radius of gyration of the chains. In the symmetric case the system spontaneously forms *lamellae* of alternating composition whose width increases as the interaction parameter does though with a weak

power law of $\chi^{1/6}$. The width of the interface region in which both A and B monomers are present decreases with χ . In a fully quantitative “strong segregation theory” of this physics (Semenov 1985), the lamellum width L and interface width w obey

$$\begin{aligned} L &= 2 \left(\frac{8}{3\pi^4} \right)^{1/6} N^{2/3} b \chi^{1/6} ; \\ w &= \frac{2b}{(6\chi)^{1/2}} . \end{aligned} \quad (28)$$

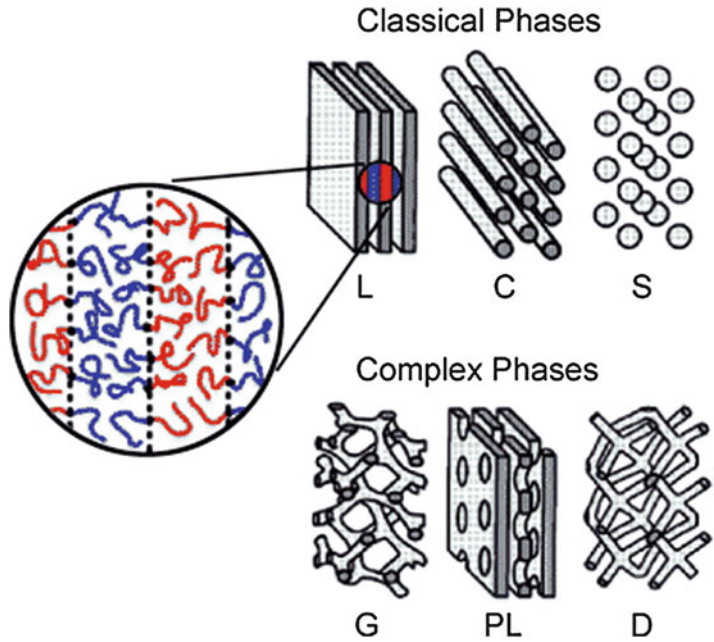
But additional physics comes into play as soon as the two blocks are of different length, for now the entropy of confinement of the chains in the plane of the interface does not balance (we did not consider that in the above), with the result that the interface tends to curve away from the domains containing the longer chains. Other more complex morphologies become candidates for the minimum in free energy: periodic cylinders (C) and spheres (S) as well as the more exotic forms of the gyroid (G), perforated lamellae (PL), and double diamond lattices (D) of Fig. 14.

Experiments on carefully synthesized block copolymers, especially the model polystyrene-polyisoprene system, have mapped out the morphology diagram in terms of interaction (via temperature, as in blends) and composition of the diblock. Calculations were first performed near the critical point, where segregation of the two species is only weak, and the free energy can be expanded in powers of the difference of the local mean concentrations $\phi = (\phi_A - \phi_B)$ (Leibler 1980), but can be extended into strong segregation by a fully continuous self-consistent mean field theory (Matsen 2002) that ignores only the fluctuations in composition. Results and comparison with experiment are shown in Fig. 15.

Clearly the calculations are qualitatively and, in some aspects, quantitatively in agreement, especially far from the disordered (fully mixed) state. However, fluctuations clearly have an important effect near the boundary. The topology of the diagram at the critical point is actually changed by them, stabilizing a finite region of the lamellar phase. Quite recently, field-theoretical methods

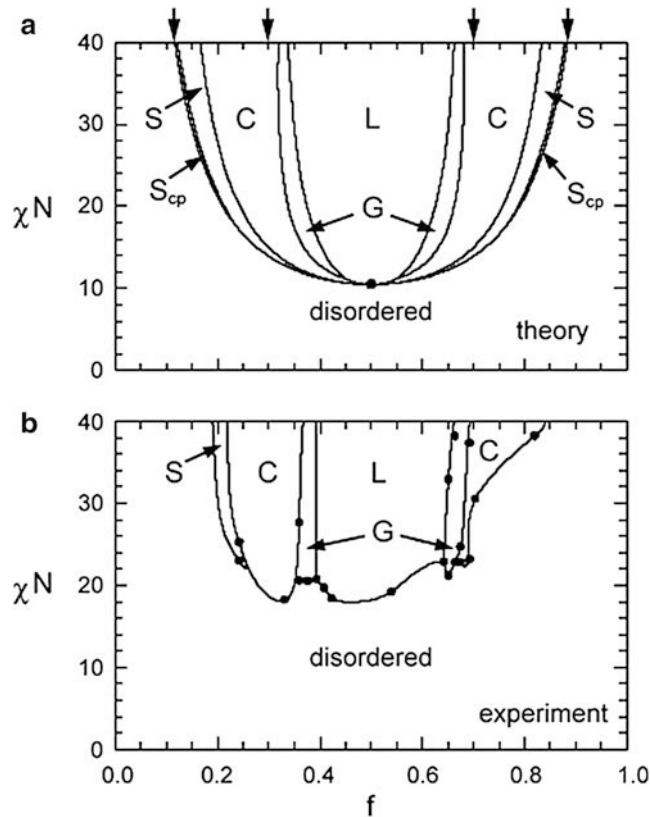
Polymer Physics,

Fig. 14 Potential candidate morphologies for block copolymer melts, from (Matsen 2002)



Polymer Physics,

Fig. 15 The morphology map for diblocks as a function of interaction parameter and composition by (a) self-consistent field calculation and (b) experiment on PS-PI diblocks. From (Matsen 2002)

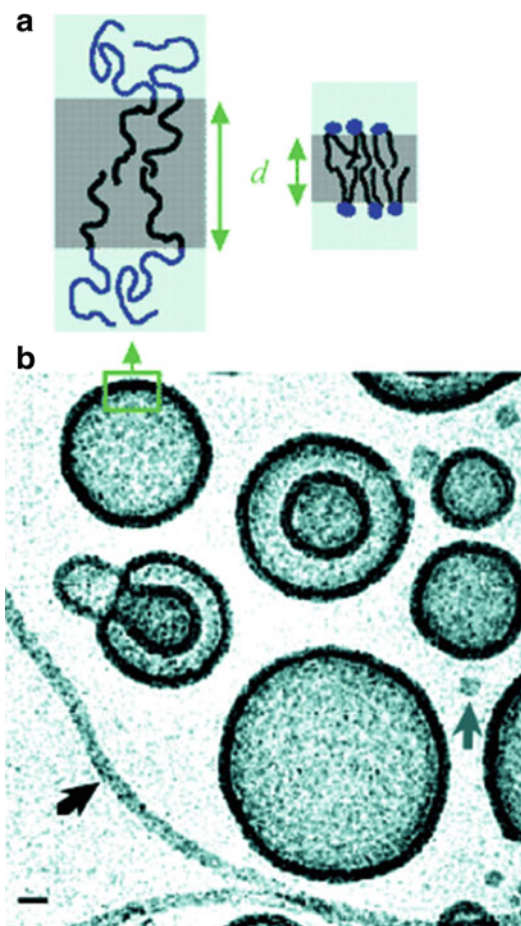


for computing the full effect of fluctuations in the partition function of block copolymers have been introduced (Fredrickson 2007). Other natural extensions include increasing the complexity of the chemical structure of the block copolymer. Taking only one step to the tri-block permits a very wide class of morphologies that mix those of the diblock, so that for example spheres of A may decorate cylinders of B within a matrix of C . Such materials are by no means only of academic interest, as they constitute the fundamental technology behind toughened plastics, in which the minority, rubbery phase prevents crack propagation within a majority glassy phase (Leibler 2005). We can begin to see the sequence of the chain corresponding to an information content (“genotype”) that implicitly codes for the morphology (“phenotype”) of the emergent morphology.

Block copolymers in solution, either of a low molecular weight species or of a simple homopolymer, may act as polymeric versions of the familiar surfactants. Their self-assembly picks out the same structures as we have already seen in the context of bulk microphase separation (lamellae, cylinders, and spheres) with now the difference that these self-assembled structures exist in isolation rather than in a regular array. The corresponding structures are vesicles, wormlike micelles, and spherical micelles (Discher and Eisenberg 2002).

Examples are given in Fig. 16. These phases have a visibly complex form, since they are largely determined kinetically: because of the long timescales for diffusion and collision of the individual micelles, and of the high activation energy for mutual rearrangement, merger, and breaking, true equilibrium is very hard to reach in these systems. So vesicles of widely different radius may coexist, together with nested structures and complexes. The transitions between linear and spherical structures, which may be driven by changes in temperature or pH depending on the chemistry of the polymers, may exhibit a rich kinetics in which cylindrical structures emerge from spherical and vice versa.

We finally consider the generalization of the coil collapse transition we saw in the case of dilute chains in poor solvents in section “Single Polymer Chain Physics.” When all monomers are identical



Polymer Physics, Fig. 16 Schematic of chain configuration in the wall of a block copolymer vesicle and its architectural control (a) and transmission electron micrograph of polymeric vesicles (b), from (Discher and Eisenberg 2002)

in their interaction with the solvent the form of the resultant globule will be on average spherical, together with natural thermal fluctuations of the interface. When the polymer contains blocks of heterogeneous interaction with solvent, as well as self-interaction, the globule may become a much more complex object. Experiments on diblocks indicate that a range of nonspherical geometries may be generated by controlling the architecture of the primary chain (Govorun et al. 2001). Calculations balancing chain stretch, mutual interaction, and surface tension against the solvent (Khokhlov et al. 2005) indicate that it is theoretically possible, using only two monomers, to code

for transitions between near-spherical to prolate and finger-like forms of the collapsed globule. More complex features such as budded and pearled structures also emerge from the same mean-field level of theory that successfully treats block copolymer melts. This single-molecule form of the coding of emergent phenotype from the information coded as a polymer sequence is very suggestive of nature's own method of constructing the functional single molecules of enzymes, motors, and cellular structures. For proteins are "just" copolymers (of a possible 20 amino acid monomer set) that code in their sequence for absolutely specific forms of their collapsed state. The protein-folding problem has generated a huge literature (Dinner et al. 2000), although rather little of it actually exploits polymer physics, with its natural high order of dimensionality and degrees of freedom (McLeish 2005) to understand this ultimate refinement of the art of coded morphology.

The complex morphologies available to liquid-liquid phase separation (LLPS) in polymeric blends, or between internally structured polymers, have likewise recently been compared to biological systems that appear to demonstrate a sort of LLPS within cells (Shin and Brangwynne 2017). There are likely to be many processes at work, recruited to deliver the internal droplets of controlled size and composition that appear to be essential to a number of biological functions, from replication and photosynthesis to cell-stress. There are indications that proteins in unfolded (or "disordered" states) are frequently at play here, suggesting that at least some of the molecular processes underlying such biological structures are shared with those of synthetic polymer physics.

Future Directions

Several current themes suggest a rich future for polymer physics, notwithstanding the experience of history that the richest veins of research to come will be those currently unforeseen. The general area of biomimetic or, perhaps better, bio-suggestive polymer physics is bound to be an

area of growth. Biology has already mastered the art of synthesizing single polymers that act as self-assembling machines, chemical reactors, and separation systems. Artificial polymers that act in these ways are certainly possible, and may not need to be as exactly structured as proteins are in order to deliver function. We have already seen that theoretical schemes exist for designing block copolymers that will collapse into predetermined shapes and forms (Khokhlov et al. 2005). Future designs of active versions of protein-like polymers may also go beyond the chemical "fuel" of ATP dephosphorylation, perhaps using light as both energy and signaling source. Optically activated mechanical transitions in polymers have already been demonstrated (Hugel et al. 2002). Effectively equally fast response can be elicited from pressure changes. In the long term one might hope for advanced therapeutics from this route, especially in combination with polymer-based encapsulation systems such as triggered micelles of block copolymers. A surprising candidate for a toolkit of nano-engineered machines and actively self-assembled polymers is DNA itself (Dunn et al. 2015). The molecule's base-pair recognition and bonding, essential for generic replication, can be recruited for designed self-assembly, while the bond energy released in forming double-stranded DNA is able to act as a sort of "fuel." This system shows considerable promise.

Structural materials properties also have many things to learn from evolution. As it becomes possible to moderate and control microstructure, both in terms of crystallinity and microseparation, so polymeric nanocomposites will be able to realize combinations of strength and stiffness currently existing as ideals (Leibler et al. 1994).

A related direction brings polymer physics into biological research directly. Dynamic neutron scattering by neutron spin echo (Bu et al. 2005), as well as advanced NMR relaxation techniques, will assist the current move toward exploring the role of dynamics in molecular biological function on a similar footing to the achievements in the area of structure. Even thermal dynamics is beginning to be recognized as a generator of functions such as signaling, in an analogous way to the emergence of rubber elasticity from the same

source (Hawkins and McLeish 2004). Technologically, the use of artificial polymers to create scaffolds for tissue engineering will require a balance of local biochemical interaction and global mechanical and topological structure formation.

The key underpinning science of biocompatible and biomimetic polymers is the control of self-assembly. Already there are a number of “supra-chemical” options of noncovalent, reversible polymerization (Lehn et al. 1990). Playing with nature’s alphabet of peptide-forming amino acids, which naturally self-assemble via main-chain hydrogen bonds, gives a rich system in which chirality becomes a new control parameter for the equilibrium structure (Davies et al. 2006). Combining main-chain self-assembly with side-chain functionality may prove to open up new classes of functional polymeric materials.

The growth of conducting and semi-conducting polymeric materials within a burgeoning new sector of the electronics industry is already well under way. But this area has been driven largely by technology, and much of fundamental science remains to be understood, especially at the level of many chain, materials physics (Barford 2005). The changing demands of the world’s energy economy are bound to put pressure on developments of organic, polymer-based photovoltaic materials, as well as lightweight polymer gel energy storage. The combination of information processing and advanced structural properties within new polymeric materials is a tempting prospect.

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Chaotic Dynamics in Nonequilibrium Statistical Mechanics

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Article Outline

Glossary

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The Roles of Ergodicity and Mixing for the
Approach to Thermodynamic Equilibrium
Integrable, Pseudo-Chaotic, and Chaotic Systems
Anosov and Anosov-Like Systems; the Chaotic
Hypothesis

Applications of Dynamical Systems Theory to
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Glossary

Chaotic systems The time evolution of a deterministic mechanical system defines a trajectory in the phase space of all the generalized coordinates and generalized momenta. Consider two infinitesimally separated points that lie on two different trajectories in this phase space. If these two trajectories typically separate exponentially with time, the system is called chaotic provided the set of all points with an exponentially separating partner is of positive measure.

Chaotic hypothesis The hypothesis that systems of large numbers of particles interacting with short ranged forces can be treated

mathematically as if the system were chaotic with no pathologies in the mathematical description of the systems' trajectories in phase space.

Dynamical systems theory The mathematical theory of the time evolution in phase space, or closely related spaces, of a deterministic system, such as a mechanical system obeying Hamiltonian equations of motion.

Ergodic systems A mechanical system is called ergodic if a typical trajectory in a phase space of finite total measure spends a fraction of its time in a set which is equal to the ratio of the measure of the set to the total measure of the phase space.

Escape rate formula Consider a chaotic dynamical system with a phase space constructed in such a way that the phase space has some kind of an absorbing boundary. The set of points, $\mathcal{R}$, in the phase space such that trajectories through them never escape through the absorbing boundary either in the forward or the backward motion is called a repeller. One can define a set of Lyapunov exponents, $\lambda_i(\mathcal{R})$ and a Kolmogorov-Sinai entropy, $h_{KS}(\mathcal{R})$ for motion on the repeller. Dynamical systems theory shows that the rate of escape, γ , of points, not on the repeller, through the boundary is given by

$$\gamma = \sum_i \lambda_i^+(\mathcal{R}) - h_{KS}(\mathcal{R}), \quad (1)$$

where the sum is over all of the positive Lyapunov exponents on the repeller.

Gaussian thermostats A dynamical friction acting on the particles in a mechanical system which keeps the total energy, or the total kinetic energy of the system at a fixed value. It was invented by Gauss as the simplest solution to the problem of finding the equations of motion for a mechanical system with a constraint of fixed energy.

Gelfand triplet An operator with right and left hand eigenfunctions, possibly defined in different function spaces, and an inner product of one function from the *right* space and one from

the *left* space. Generally, one of these spaces contains singular functions such as Schwartz distributions and the other contains sufficiently smooth functions so that the inner product is well defined. The term *rigged Hilbert space* is also used to denote a Gelfand triplet.

Hyperbolic dynamical system A chaotic system where the tangent space to almost all trajectories in its phase space can be separated into well-defined stable and unstable manifolds, that intersect each other transversally.

Kolmogorov-Sinai entropy per unit time A measure of the rate at which information about the initial point of a chaotic trajectory is produced in time. The exponential separation of trajectories in phase space, characteristic of chaotic motion, implies that trajectories starting at very close-by, essentially indistinguishable, initial points will eventually be distinguishable. Hence as time evolves we can specify more precisely the initial point of the trajectory. Pesin has proved that for closed, hyperbolic systems, the Kolmogorov-Sinai entropy is equal to the sum of the positive Lyapunov exponents. The Kolmogorov-Sinai entropy is often called the metric entropy.

Lyapunov exponent Lyapunov exponents, λ_i , are the rates at which infinitesimally close trajectories separate or approach with time on the unstable and stable manifolds of a chaotic dynamical system. For closed phase spaces, that is, no absorbing boundaries present, Pesin theorem states that for hyperbolic dynamical system the Kolmogorov-Sinai entropy, h_{KS} is given by the sum of all the positive Lyapunov exponents.

$$h_{KS} = \sum_i \lambda_i^+. \quad (2)$$

Mixing systems Mixing systems are dynamical systems with stronger dynamical properties than ergodic systems in the sense that every mixing system is ergodic, but the converse is not true. A system is mixing if the following statement about the time development of a set A at t is satisfied

$$\lim_{T \rightarrow \infty} \frac{\mu(A_T \cap B)}{\mu(B)} = \frac{\mu(A)}{\mu(\mathcal{E})}, \quad (3)$$

where B is any set of finite measure, and $\mu(\mathcal{E})$ is the measure of the full phase space. This statement is the mathematical expression of the fact that for a mixing system, every set of finite measure becomes uniformly distributed throughout the full phase space, with respect to the measure μ .

Normal variables Microscopic variables whose values are approximately constant on large regions of the constant energy surface in phase space.

Pseudo-chaotic systems A pseudo-chaotic system is a dynamical system where the separation of nearby trajectories is algebraic in time, rather than exponential. Pseudo-chaotic systems are weakly mixing as defined by the relation

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T d\tau \left[\mu(A_\tau \cap B) - \frac{\mu(A)\mu(B)}{\mu(\mathcal{E})} \right] = 0. \quad (4)$$

Sinai-Ruelle-Bowen (SRB) measure SRB measures for a chaotic system are invariant measures that are smooth on unstable manifolds and possibly singular on stable manifolds.

Stable manifold A stable manifold about a point P in phase space is the set of points that will approach P at time t approaches positive infinity, that is in the infinite future of the motion.

Transport coefficients Transport coefficients characterize the proportionality between the currents of particles, momentum, or energy in a fluid, and the gradients of density, fluid velocity or temperature in the fluid. The coefficients of diffusion, shear and bulk viscosity, and thermal conductivity are transport coefficients, and appear as coefficients of the second order gradients in the Navier-Stokes and similar equations.

Unstable manifold An unstable manifold about a point P in phase space is the set of points that will approach P as time approaches negative infinity, that is, as one follows the motion backwards in time to the infinitely remote past.

Definition of the Subject

For most of its history, non-equilibrium statistical mechanics has produced mathematical descriptions of irreversible processes by invoking one or another stochastic assumption in order to obtain useful equations. Central to our understanding of transport in fluids, for example, are random walk processes, which typically are described by stochastic equations. These in turn lead to the Einstein relation for diffusion, and its generalizations to other transport processes. This relation, as formulated by Einstein, states that the mean square displacement of a diffusing particle grows linearly in time with a proportionality constant given by the coefficient of diffusion. If we assume that such a description applies to mechanical systems of many particles, we must explain the origins of irreversibility in deterministic – and time reversible – mechanical systems, and we must locate the source of stochasticity that is invoked to derive transport equations. For systems of particles that are chaotic, it is possible to make some progress on resolving these issues, and to gain some insights into the analogous properties of systems that are not chaotic or that have both chaotic and non-chaotic behaviors. This article summarizes the current status of the application of dynamical systems theory to non-equilibrium statistical mechanics, focuses on the behavior of chaotic systems, and presents some of the important open issues needing resolution.

Introduction

Statistical mechanics is devoted to the study of the collective properties of large numbers of particles, typically atoms, molecules, electrons, etc., but can also be stars, or even galaxies. The mechanical properties of the individual particles and their mutual interactions are presumed to be known, and the emphasis is on the statistical properties of collections of large numbers of them (Uhlenbeck and Ford 1963; Toda et al. 1992; Kubo et al. 1992). The study of statistical mechanics has always involved both an examination of its foundations and the devising of methods to compute thermodynamic, transport, and related

quantities for systems of large numbers of particles. In recent years, there has been a great deal of attention focused on the foundations of statistical mechanics prompted by developments in: (i) dynamical systems theory, particularly chaotic dynamics, (ii) the mathematics of Anosov and hard-ball systems, and in (iii) the computational physics of systems of particles undergoing processes of various kinds (Eckmann and Ruelle 1985; Evans and Morriss 1990; Gaspard 1998; Hoover 1999; Dorfman 1999; Ruelle 1999; Gallavotti 1999; Szasz 2000; Klages 2007; Klages et al. 2004; Katok and Hasselblatt 1995). Moreover, modern developments in quantum physics, particularly those of some relevance for the foundations of quantum mechanics, for cosmology, and for quantum computation have some bearing on the foundations of quantum statistical mechanics (Srednicki 1999).

Non-equilibrium statistical mechanics is faced with the task of describing the wide range of non-thermodynamic, generally time-dependent behaviors of large systems, such as the transport of particles, momentum, and/or energy from one region in space to another over some time interval. Despite a large number of, as yet, unsolved problems, non-equilibrium statistical mechanics has been able to explain and provide quantitative predictions for a wide range of transport phenomena. Here we will discuss some of these applications and describe the role played by the microscopic dynamics of the constituent particles, particularly when the microscopic dynamics is classical and chaotic (Katok and Hasselblatt 1995). Most of this article will be devoted to a study of the role of chaotic dynamics in non-equilibrium transport for classical, chaotic systems. We will also consider, to some extent, classical, non-chaotic systems as well as quantum systems, where the usual notions of chaotic dynamics do not apply but one can nevertheless understand some main features of the behavior of a quantum system by examining its classical counterpart, if there is one.

This article is devoted to the role played by chaotic dynamics in our understanding non-equilibrium statistical mechanics. It will focus on two main topics: (1) Basic issues in statistical mechanics, namely, the approach of systems of

particles to thermodynamic equilibrium. Here we give an updated view of the role of ergodic and mixing properties, proposed by Boltzmann and Gibbs, respectively, as the basis for understanding the approach to equilibrium (Uhlenbeck and Ford 1963; Toda et al. 1992; Kubo et al. 1992; Eckmann and Ruelle 1985). (2) Applications of dynamical systems theory to non-equilibrium statistical mechanics and the theory of transport processes. Here we show that for chaotic systems, at least, one can find some very deep relationships between macroscopic transport and microscopic dynamics (Evans and Morriss 1990; Gaspard 1998; Hoover 1999; Dorfman 1999; Ruelle 1999; Gallavotti 1999; Szasz 2000; Klages 2007; Klages et al. 2004). We also discuss, briefly, the closely related topic of fluctuation theorems for non-equilibrium stationary states which apply even in far-from equilibrium situations (Evans et al. 1993; Evans and Searles 2002; Gallavotti and Cohen 1995; Lebowitz and Spohn 1999; Crooks 1999; Kurchan 1998).

By way of introduction we begin with some observations about transport processes in fluids in order to set the stage for describing the role of chaotic dynamics in transport theory. As we will discuss in more detail below, normal transport processes in fluids are characterized by a linear growth in time of the mean square fluctuations of an appropriate time dependent microscopic variable of the system. Typical of such a fluctuation formula is the Einstein relation which states that the mean square displacement of a particle undergoing Brownian motion in a fluid grows linearly in time with a coefficient that is, apart from a numerical factor, the diffusion coefficient of the Brownian particle (Mazo 2002). That is

$$\langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle = 2dDt. \quad (5)$$

Here $\mathbf{r}(t)$ is the spatial location of the Brownian particle at some time t , and d is the number of spatial dimensions of the system. D is the diffusion coefficient appearing in the linear relation, known as Fick's Law, that relates the probability current, $\mathbf{J}(\mathbf{r}, t)$ for the Brownian particle to its probability density, $P(\mathbf{r}, t)$,

$$\mathbf{J}(\mathbf{r}, t) = -D\nabla P(\mathbf{r}, t). \quad (6)$$

The angular brackets denote an average over an ensemble of trajectories of time duration t , at least. At the heart of the Einstein formula is the fact that the Brownian particle undergoes a random walk on sufficiently long-time scales. The distinguishing feature of a random walk is the linear growth in time of the mean square displacement. Thus, normal transport in general is a form of a random walk process. This was formalized by Helfand in 1960 (Helfand 1960), who generalized the Einstein formula to other transport processes such as viscous flow, and heat conduction. By normal transport we mean transport that can be described macroscopically by linear relations between the currents of globally conserved quantities such as mass, energy, and/or momentum, and the gradients of the densities of these quantities. The coefficients of proportionality are transport coefficients, such as the coefficients of shear and bulk viscosity, thermal conductivity, diffusion, and so on. These coefficients, for normal transport, do not depend on time, but may depend on the local densities of mass and the local temperature of the fluid.

Helfand was able to show that each transport process may be regarded as a random walk process characterized by a linear growth as a function of time of the mean square fluctuation of a microscopic quantity, $M_\sigma(\Gamma, t)$, called a Helfand moment. The Helfand moments depend on all of the phase space variables of the system, now denoted collectively by Γ , and time t . For normal transport, the generalized Einstein relation becomes

$$\langle (M_\sigma(\Gamma, t) - M_\sigma(\Gamma, t=0))^2 \rangle = \sigma C_\sigma t. \quad (7)$$

Here σ is a transport coefficient appearing in the Navier-Stokes or diffusion equations, C_σ is a constant, and the average is over an equilibrium ensemble. For diffusion of a Brownian particle, for example, the Helfand moment is simply the spatial location of the particle. This result implies that normal transport processes are essentially random walk processes with a generalized "displacement," namely, the Helfand moment.

If we think of a system of particles, undergoing some kind of hydrodynamic flow as a deterministic dynamical system, with, typically but not exclusively, Hamiltonian dynamics, a deep question immediately presents itself: *Where does the randomness come from that is required for transport processes to be generalized random-walk processes?* While there are a variety of answers to this question, the main point of this article is to argue that for *chaotic systems* the randomness is an intrinsic property of the dynamics of the system (Katok and Hasselblatt 1995), and then to illustrate some of the results that have been obtained recently which connect microscopic dynamics to macroscopic transport for such systems. We emphasize that many chaotic systems display the kind of randomness needed for good transport properties even though such systems are deterministic, and time reversible. However, chaos is neither necessary nor sufficient for normal transport. There are examples of non-chaotic systems that exhibit normal diffusion. The wind-tree model to be discussed below is an example (Ehrenfest and Ehrenfest 1959; Dettmann and Cohen 2000). There are also chaotic systems that exhibit abnormal transport. The two-dimensional periodic Lorentz gas with circular scatterers is chaotic and exhibits both normal and abnormal diffusion, depending upon the lattice structure and the separation distance between neighboring scatterers (Bunimovich and Sinai 1981; Gaspard and Baras 1995).

Nevertheless, chaotic systems have sufficiently many nice properties that for them it is possible to obtain a number of rather, general connections between microscopic dynamics and macroscopic transport, and to understand the approach of systems to thermodynamic equilibrium from a dynamical standpoint. Such connections, should they exist, are not yet available for those non-chaotic systems which exhibit normal transport. The dynamical properties of most non-chaotic systems are not yet sufficiently well understood for the construction of a more or less general theory for generic connections between microscopic dynamics and macroscopic transport. Most realistic dynamical systems have a *mixed* phase space, where chaotic and non-chaotic regions, to be defined below, are intermingled

(Turaev and Rom-Kedar 1998; Donnay 1996). It is generally supposed that for systems of large numbers of particles in macroscopic volumes, the non-chaotic regions occupy a very small part of phase space and can be ignored for all practical purposes. However, this remains to be proved, and the effects of the non-chaotic regions require much more elucidation.

The plan of this article is as follows: We begin with a discussion of the foundations of statistical mechanics in section “[The Roles of Ergodicity and Mixing for the Approach to Thermodynamic Equilibrium](#).” There we discuss dynamical properties that are often considered to be important for statistical mechanics, such as ergodicity and mixing. There we argue that these properties, by themselves, are not sufficient to explain the approach to equilibrium of systems of large numbers of particles and that further notions are required. This will lead us in section “[Integrable, Pseudo-chaotic, and Chaotic Systems](#)” to a discussion of some of the dynamical systems encountered in classical statistical mechanics, particularly integrable, pseudo-chaotic, and chaotic systems. In section “[Anosov and Anosov-Like Systems; the Chaotic Hypothesis](#),” we consider chaotic systems in more detail and show for a simple model of a chaotic system that the stochastic behavior needed for diffusion can be seen as a natural consequence of chaotic dynamics. Despite its simplicity and low dimensionality, this model will also allow us to provide a dynamical picture of the approach of a system to equilibrium. These models are simple examples of classes of dynamical systems called Anosov and Anosov-like systems. They have very useful mathematical properties for the description of non-equilibrium phenomena in simple systems, and it is convenient to assume, whenever possible, that the systems of interest to physicists have these good properties. These properties are then used for the applications of chaotic dynamics to non-equilibrium statistical mechanics in section “[Applications of Dynamical Systems Theory to Non-equilibrium Statistical Mechanics](#).” There we discuss a number of results that connect microscopic dynamical properties such as Lyapunov exponents and Kolmogorov-Sinai entropies

(Eckmann and Ruelle 1985; Evans and Morriss 1990; Gaspard 1998; Hoover 1999; Dorfman 1999; Ruelle 1999; Gallavotti 1999; Szasz 2000; Klages 2007; Klages et al. 2004; Katok and Hasselblatt 1995) to macroscopic transport coefficients for chaotic systems. In section “[Discussion](#)” we review the previous discussion and give brief comments about quantum systems, where the concepts of classical chaotic dynamics do not apply, but certain features of these systems can be understood in terms of the chaotic dynamics of their classical counterparts. Finally, we mention some future directions and open questions in section “[Future Directions](#).”

The Roles of Ergodicity and Mixing for the Approach to Thermodynamic Equilibrium

Ergodic Systems

Boltzmann invented the notion of ergodicity in an attempt to reconcile the apparently irreversible behavior of large systems of particles, especially their approach to thermodynamic equilibrium, with the microscopic reversibility of Newton’s equations of motion (Uhlenbeck and Ford 1963; Toda et al. 1992; Kubo et al. 1992). Briefly put, Boltzmann argued as follows: Consider an isolated system of particles and follow the system’s trajectory on the appropriate constant energy surface in phase space. Suppose that the underlying microscopic dynamics of the system is such that the phase space trajectory of the system, over a long time interval, spends an amount of time in every region of phase space, A , that is proportional to the measure of that region, $\mu(A)$. Here the measure is the standard equilibrium phase space measure on a constant energy surface given by

$$\mu(A) = \int_A \frac{dS}{|\nabla H|}, \quad (8)$$

where dS is the area of an infinitesimal region of the constant energy surface, and $|\nabla H|$ is the magnitude of the gradient of the Hamiltonian function for the system at the point of integration. Boltzmann’s supposition above is called the

ergodic hypothesis, and in mathematical terms it can be stated as (Eckmann and Ruelle 1985)

$$\lim_{T \rightarrow \infty} \frac{\tau(A)}{T} = \frac{\mu(A)}{\mu(\mathcal{E})}. \quad (9)$$

Here $\tau(A)$ is the amount of time the system spends in region A during a time interval T , and $\mu(\mathcal{E})$ is the measure of the entire constant energy surface, which we assume to be finite. If one accepts the hypothesis, then one can easily show, by approximating integrals by sums, for example, that the *time average* of any well-behaved dynamical quantity approaches its equilibrium, microcanonical ensemble average as the time interval over which the average is taken approaches infinity. Boltzmann’s hypothesis holds equally well for the time reversed motion of the system and is consistent with the reversibility of the microscopic dynamics.

The kinds of elementary physical systems one studies in physics courses, such as coupled systems of harmonic oscillators, are generally not ergodic, although some simple systems, such as a single, one dimensional harmonic oscillator, can be shown to be ergodic. Another simple example is the discrete time motion of a point particle on the circumference of a circle, where the particle moves a fixed irrational fraction of the length of the circumference at successive time steps. In the long-time limit, the circumference is uniformly covered by points visited by the particle (Walters 1982). A great deal of mathematical research over the past few decades, and longer, has been devoted to a study of more complicated ergodic systems. The first dramatic example of a system with ergodic properties, and one that has influenced most of the more recent efforts in this direction is the geodesic motion of a point on a surface of constant negative curvature. This was proved by E. Hopf (1937), and the techniques employed remain useful today. Sinai and coworkers (Sinai 1991), as well as many other workers, particularly Simányi (2004), have given careful mathematical proofs of ergodic behavior of various systems composed of hard disks or hard spheres, generally referred to as hard-ball systems. Turaev and Rom-Kedar, Donnay and others

(Turaev and Rom-Kedar 1998; Donnay 1996) have shown that by softening the hard sphere potential one may change an ergodic system into a non-ergodic one. Thus, the problem of proving that a system of interest to physicists is actually ergodic, or ergodic for practical purposes, is still far from a general solution.

Mixing Systems

Gibbs took a different approach to the problem of irreversibility. He used the analogy of an ink drop being stirred in a container of glycerin to introduce the stronger notion of a *mixing system* in his efforts to understand the approach of a non-equilibrium ensemble distribution function to an equilibrium distribution (Eckmann and Ruelle 1985; Dorfman 1999). In considering a non-equilibrium phase space distribution one has to follow the trajectories of a set of points in phase space, not just a typical trajectory, as in the study of ergodic behavior. Gibbs suggested that an initial set of points concentrated in a small region of phase space might spread out over the entire available phase space in the course of time, and become finely mixed throughout the phase space in much the same way as the ink drop will become mixed in the glycerin, in such a way that a coarse grained observation of the ink would lead to the conclusion that it is uniformly mixed, but a fine grained observation would reveal the individual threads of ink. Returning to phase space, Gibbs argued that although the measure of phase space occupied by the set of points should remain constant in time, in accordance with Liouville's theorem, the set eventually gets distributed over the constant energy surface such that a coarse grained observation of the phase space would lead to the conclusion that the set uniformly covers the energy surface, while a fine grained observation would reveal that the coverage consists of one long, thin set of total measure much less than that of the whole energy surface. Of course, mechanical reversibility ensures that one can recover the initial distribution of points by time reversing the motion but eventually mixing takes place for the time reversed motion, as well.

The mathematical definition of a mixing system (Walters 1982) is given by looking at the time

development of the initial set of phase points. We denote by A , the initial set of phase points on which the initial ensemble is concentrated, and the set to which this initial set evolves after a time T , by A_T . Then, to examine the mixing of the set in phase space, we consider some arbitrary set of positive measure B and consider the intersection $B \cap A_T$. If the dynamics of the system is mixing, then eventually the fraction of the set B occupied by A_T should approach the fraction of A in the entire phase space, no matter what sets of positive measure A and B we consider. That is, a system is mixing if for any sets A and B of positive measure

$$\lim_{T \rightarrow \infty} \frac{\mu(A_T \cap B)}{\mu(B)} = \frac{\mu(A)}{\mu(\mathcal{E})}. \quad (10)$$

Here we used the conservation of phase space measure, namely, that $\mu(A) = \mu(A_T)$. One can easily prove that a mixing system is also ergodic, but the reverse need not be true (Walters 1982).

For a system of particles with the mixing property one can prove that a non-equilibrium phase space distribution will approach an equilibrium phase space distribution in a *weak*, long time limit (Dorfman 1999). That is, average quantities taken with respect to the non-equilibrium distribution approach equilibrium averages. The proof can easily be constructed by approximating integrals by sums in the usual way.

Mathematicians have considered proofs of the mixing property for various systems of interest to physicists. The most important of such systems are hard ball systems mentioned previously, where the proofs of ergodicity and mixing are consequences of proving a stronger dynamical property, the Bernoulli property of the system, which implies that the system is mixing and therefore ergodic as well. We leave a proper definition of a Bernoulli system to the literature (Cornfeld et al. 1982) and we will not consider it any further here. Needless to say, the class of systems which can be proved to be mixing is not yet large enough to encompass the typical systems studied in statistical mechanics or in kinetic theory, although considerable progress has been made in this direction over the past several years.

What Is the Relevance of These Notions for Statistical Mechanics?

It would appear that with the proof that a system of a large number of particles in a reasonable container is mixing, the foundation for the applications of statistical mechanics to such a system would be secure. That this is not a complete explanation may be seen for the following reasons, among others:

1. We have assumed that our systems have fixed energies and that all the forces acting between the particles or on the system, due to the walls of the container, say, are conservative and known. Strictly speaking, this is not true of any laboratory system.
2. We have not examined how long it might take for the time average to be reasonably close to the ensemble average for an ergodic system or how long it would take a reasonable initial set to get uniformly mixed over the appropriate phase space, for a mixing system. One can argue that the appropriate times are very long, typically very much longer than the duration of an experiment. A partial but useful answer to this objection to the use of ergodicity and/or mixing properties is to consider Reduced distribution functions, particularly the single particle and two-particle distribution functions. These reduced distribution functions approach equilibrium, or more generally, local equilibrium forms, on much more realistic time scales.

The notion of local equilibrium arises in the context of the decay of a non-equilibrium state in a many particle system to total equilibrium, through hydrodynamic processes. In the usual picture, due to Chapman, Enskog, and Bogoliubov (Chapman and Cowling 1970; Bogoliubov 1962), the initial state becomes, on the time scale of the duration of a collision, one that can be described by reduced distribution functions. Then on the time scale of the time between collisions, set by the microscopic properties of the system such as the density and the size of the particles, the system becomes close to a state of local equilibrium with a local temperature, density and mean velocity. Finally, on a time scale set by the physical

size of the container, the system relaxes to total equilibrium. The approach to local equilibrium is set by the dynamical interactions between the particles.

In addition, many non-equilibrium as well as equilibrium properties of a many-particle system can be formulated in terms of these reduced functions. This being the case, the questions are: What is the reason that reduced distribution functions approach local equilibrium forms, and what are the time scales involved in the approach to local equilibrium, and eventually to total equilibrium? For chaotic systems, at least, there is reason to believe that one can provide satisfactory answers to these questions.

Another approach to resolving the issue of time scales in applying these notions to laboratory systems, and one closely related to the use of reduced distribution functions is to focus attention on a set of microscopic variables called *normal variables* (Uhlenbeck and Ford 1963). These variables are defined by the requirement that they not vary much over the constant energy surface. These variables then have the property that their value is almost the same no matter where the phase point happens to be on the constant energy surface. In this picture an initial non-equilibrium state would be one where the values of the normal variables are far from their equilibrium or average values, but the time evolution of the system leads to regions where these variables have values closer to their equilibrium averages. In this picture the relevant time scale is the average time needed for the system to evolve to regions of phase space where the normal variables are close to their average values. Presumably this time will be much shorter than the time needed for the trajectory to cover the phase space. However, we need a detailed description of these variables and a description of their behavior as a system approaches local, then total equilibrium via kinetic and hydrodynamic processes, respectively. In the absence of such an understanding of normal variables, in general, the reduced distribution functions provide a clearer way to address the questions

of time scales for the approach of distribution functions to their equilibrium values.

One can imagine, that both the reduced distribution resolution and the normal variable resolution of the time scale issue become easier to justify as the number of degrees of freedom, or the number of particles become large. In either case, although the phase space measure will also grow, and the time needed to cover it will increase, the relative fluctuations in the reduced distribution functions and normal variables will become smaller. It should be emphasized that the notions of ergodicity and mixing have an important role to play in statistical mechanics, despite the issues raised here concerning the time needed for covering the full phase space. Using ergodicity one can motivate the use of the micro-canonical ensemble and ultimately all of the Gibbs ensembles that provide methods for computing equilibrium properties of systems. Similarly, the mixing property can be used to show that time correlation functions decay in time, an important property needed for many applications of non-equilibrium statistical mechanics, particularly for the Green-Kubo formalism (Toda et al. 1992; Kubo et al. 1992).

3. We have used classical mechanics as our description of dynamics, but nature is fundamentally quantum mechanical.

In the following sections we will address point (2) in some detail, and point (3), briefly. It is important to note, however, that the answers we shall provide, while encouraging, are very incomplete and much more work needs to be done to make these answers believable and secure. Here we consider point (1). As mentioned in the previous section, in order to produce a random walk of the Helfand moments needed for normal transport, some sort of stochastic or stochastic-like mechanism is required. Possible sources of stochastic behavior could be random external influences or some built-in structural randomness, however subtle and difficult to identify. Evidence for the effectiveness of built-in randomness is provided by a useful model of a statistical system, such as the Ehrenfest wind-tree model (Ehrenfest

and Ehrenfest 1959), where diamond shaped scatterers (trees) are placed at random in a plane, with their diagonals aligned parallel to the x - and y -axes. Then point particles (wind) move among the trees with velocities only in the $\pm x$ and $\pm y$ directions. The random placement of the trees provides a clear stochastic mechanism leading to normal diffusion and an approach to equilibrium and thereby simulate a mixing system. Such systems are not chaotic and some source of randomness beyond the dynamics is necessary for normal transport in such non-chaotic models. Moreover, there are periodic versions of the wind-tree model that also exhibit normal diffusion (Klages 2007; Dettmann and Cohen 2000), with more subtle sources of randomness, possibly connected with the splitting of two nearby trajectories at the corners of the scatterers. Below we turn our attention to the case of chaotic systems and argue that for such systems, the dynamics can be enough to allow normal transport and the approach of an ensemble of such systems to equilibrium, even when the system is spatially periodic.

Integrable, Pseudo-Chaotic, and Chaotic Systems

The kind of systems one studies in courses on classical mechanics are typically *integrable system*. These are systems with N canonical coordinates, N canonical momenta, and N independent constants of the motion (Toda et al. 1992). The canonical coordinates of such systems can be transformed to a set of action-angle variables, and when expressed in these variables, the systems become quasi-periodic in time, and the motion is confined to regions in phase space called invariant tori. Systems of coupled harmonic oscillators are good examples of integrable systems. There is another class of mechanical systems, of which the Ehrenfest wind-tree model described above is an example, called *pseudo-chaotic* systems (Zaslavsky 2007). These systems have the property that two infinitesimally close trajectories will separate algebraically with time, for sufficiently long times. For example, two distinct trajectories moving in initially

parallel directions in a wind-tree system will eventually separate algebraically with time, no matter how close they are to each other initially, due to the random placement of scatterers and the fact that one of the two trajectories will eventually hit a scatterer that is “just missed” by the other one. Pseudo-chaotic systems have a *weak mixing* property (Walters 1982; Zaslavsky 2007), namely, that

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T d\tau \left[\mu(A_\tau \cap B) - \frac{\mu(A_\tau)\mu(B)}{\mu(E)} \right] = 0. \quad (11)$$

Chaotic systems are usually defined by the condition that two infinitesimally close trajectories will, in the appropriate long time limit, separate exponentially (Eckmann and Ruelle 1985). We will give a more careful discussion of chaotic systems in the next section.

Anosov and Anosov-Like Systems; the Chaotic Hypothesis

Earlier in this discussion we argued that the notions of ergodicity and mixing are not, in themselves, fully sufficient for understanding the approach to thermodynamic equilibrium for systems of many particles due to problems of time scales. In addition, we argued that in many cases reduced distribution functions may very well be better indicators of the approach to equilibrium than the full phase space distribution function. We also suggested that for chaotic systems at least, these observations can be verified to the extent

that we can make some more detailed statements concerning the approach to equilibrium and transport properties. Here we will provide some justification for these comments.

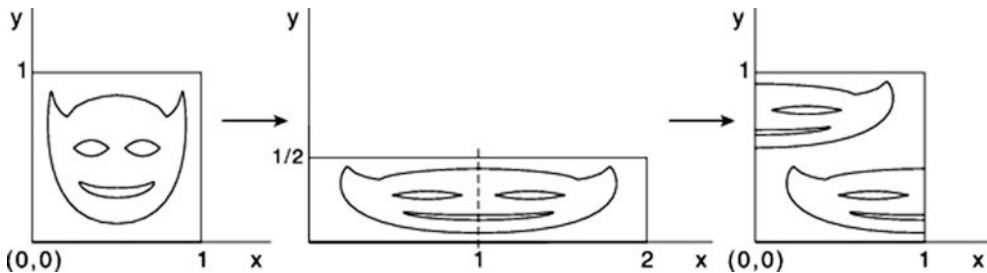
It is helpful to consider simple model systems that display the kind of irreversible behavior that we would like to be able to describe for more realistic, many particle systems. Two model systems that have this feature are the baker’s map (Hopf 1937; Berry 1978) and the Arnold Cat Map, which itself is an example of more general models called hyperbolic toral automorphisms (Katok and Hasselblatt 1995). We will explain this terminology as we proceed.

The baker’s map is a map of a two dimensional “unit square,” $0 \leq x, y \leq 1$ onto itself, given by (see Fig. 1)

$$\begin{aligned} \begin{pmatrix} x' \\ y' \end{pmatrix} &= \begin{pmatrix} 2x \\ y/2 \end{pmatrix} \quad \text{for } 0 \leq x \leq 1/2; \\ \text{and } &= \begin{pmatrix} 2x - 1 \\ (y + 1)/2 \end{pmatrix} \quad \text{for } 1/2 < x < 1. \end{aligned} \quad (12)$$

This map consists of a stretching of the square in the x -direction by a factor of 2 and squeezing in the y -direction by a factor of 1/2. The elongated image of the unit square is then cut in half and the right side is put on top of the left side so that a unit square is reconstructed, after each application of the map. Of course, this is an area preserving map, and it has a discontinuity at $x = 1/2$.

Suppose the x, y -plane is our (two-dimensional) phase space and the motion of a



Chaotic Dynamics in Nonequilibrium Statistical Mechanics, Fig. 1 The baker’s map: The unit square is mapped onto itself by stretching by a factor 2 in the

x -direction and by a compression by a factor of 1/2 in the y -direction. This is followed by cutting and re-arranging the resulting rectangle

phase point is confined to the unit square. We now apply some of the usual techniques of statistical mechanics to baker-map distribution functions defined on the unit square. The phase space distribution function changes at each time step according to

$$\begin{aligned} \rho_n(x, y) &= \rho_{n-1}(x/2, 2y) \text{ for } 0 \leq y \leq 1/2; \\ \text{and } \rho_n(x, y) &= \rho_{n-1}((x+1)/2, 2y-1) \text{ for } 1/2 < y < 1. \end{aligned} \quad (13)$$

For statistical mechanics, we often are interested in the reduced distribution functions of fewer variables. Here there are only two variables, so we consider the reduced distribution function, $W_n(x)$ obtained by integrating $\rho_n(x, y)$ over the y coordinate. Using Eq. (13), we obtain the equation (Berry 1978)

$$W_n(x) = \frac{1}{2} \left[W_{n-1}\left(\frac{x}{2}\right) + W_{n-1}\left(\frac{x+1}{2}\right) \right]. \quad (14)$$

If one assumes that the initial value, $W_0(x)$, of the reduced distribution function is a reasonably smooth function of x , for example, if it can be represented by a convergent Fourier series, then $W_n(x)$ approaches a constant value as $n \rightarrow \infty$! The reason for this is that Eq. (14) says that the reduced distribution at time n at a point x is the average value of the distribution at two points, $x/2$ and $(x+1)/2$ at the previous time, $n-1$. This averaging, if carried on long enough, produces a function which is constant in x . One can readily estimate the time it takes to reach this uniform state in the following way. Suppose that $l < 1$ is some length scale on which $W_0(x)$ varies with x . Then since the baker's map stretches sets of length l into sets of length $2l$ we can estimate the time to reach equilibrium as the time it takes a set of length l to be stretched to a set of length 1, which is $(-\ln l)/(\ln 2)$. This can be much shorter than the time it takes for the ergodic or mixing properties of the baker's map to make themselves manifest, which takes an additional time of order $\ln N / \ln 2$ to produce N horizontal strips of unit length, stacked in the y -direction. If we were to consider the reduced distribution function in the y variable, we would not get a nice equation with a

distribution function that approaches equilibrium. Why that is so will be clear in a moment.

We have not introduced any stochastic features into our derivation of Eq. (14), but only integrated the Liouville equation over one of the variables. Thus, we have been able to start from the Liouville equation, and by introducing nothing but an initial condition and integrating over the appropriate number of unmeasured variables, obtain an irreversible equation for a reduced distribution function which approaches equilibrium. Incidentally, the quantity $S = -\int_0^1 dx W_n(x) \ln W_n(x)$ exhibits a monotonic increase with time n (Dorfman 1999).

Our analysis of the approach to equilibrium of the function $W_n(x)$ made strong use of the stretching nature of the map in the x -direction. To get some further insight into the importance of the stretching of the phase space regions, we consider another model, the Arnold Cat Map (Katok and Hasselblatt 1995) (see Fig. 2). Here the unit square, with opposite sides identified, represents a torus. This transformation maps the torus (that is, there is no cutting and moving of any section as there is in the baker's map) onto itself and may be described by a 2×2 matrix with unit determinant and integer elements. Such maps are called *toral automorphisms* (Katok and Hasselblatt 1995), of which the Cat Map is a specific example. This map has an additional, *hyperbolic*, property, namely, that one of its eigenvalues be greater than unity. It follows from the fact that the determinant is unity, that the other eigenvalue is less than unity, and the product of the two is 1. The standard version of the map is given by the symmetric matrix

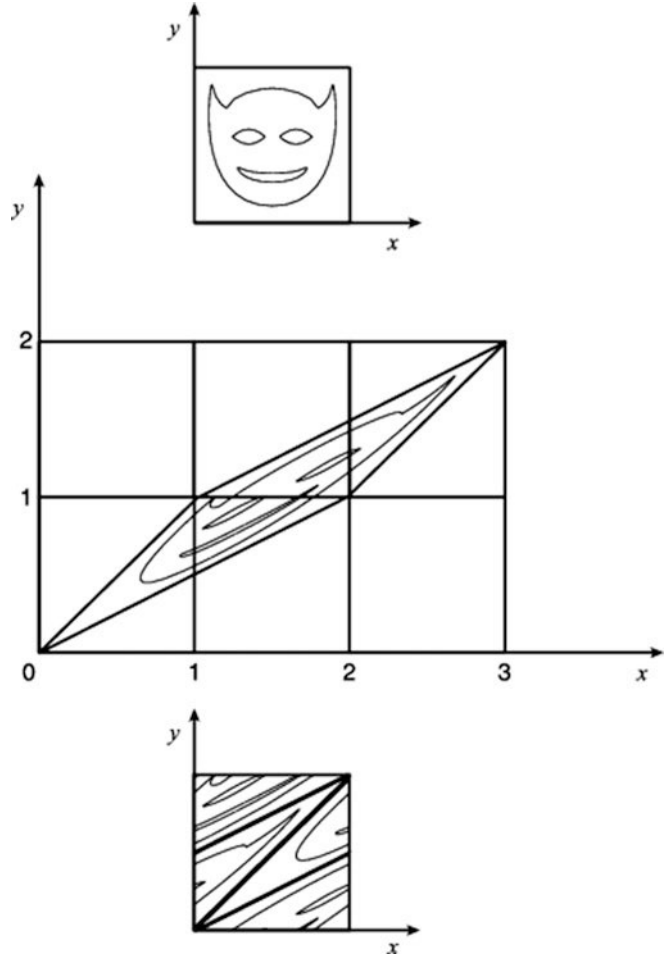
$$\begin{aligned} \begin{pmatrix} x' \\ y' \end{pmatrix} &= \mathbf{T} \cdot \begin{pmatrix} x \\ y \end{pmatrix} \\ &= \begin{pmatrix} 2 & 1 \\ 1 & 1 \end{pmatrix} \cdot \begin{pmatrix} x \\ y \end{pmatrix}, \text{ modulo } 1. \end{aligned} \quad (15)$$

The eigenvalues of $\mathbf{T}$ are $(3 \pm \sqrt{5})/2$. The eigendirections are perpendicular to each other and make non-zero angles with the x - and y -axes. There is a stretching direction which corresponds to the direction of the larger eigenvalue,

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Fig. 2 The Arnold Cat Map of the unit torus onto itself



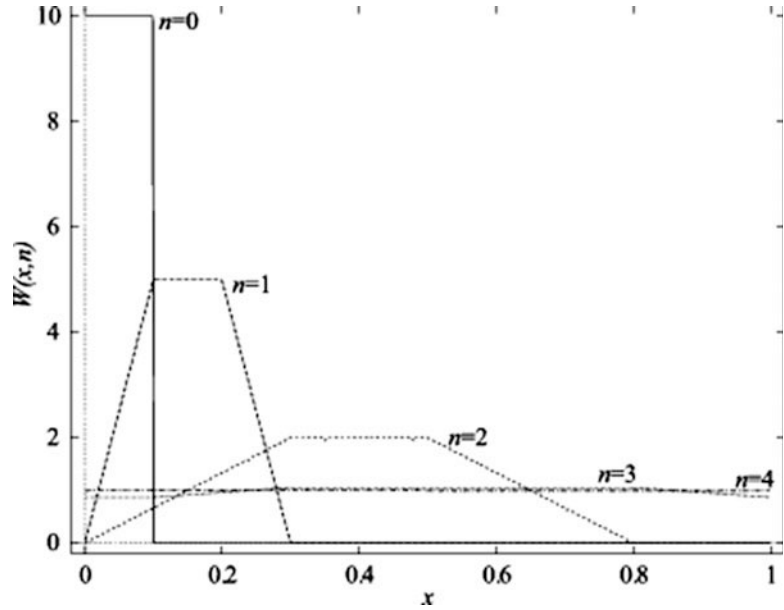
and a contracting direction which corresponds to the smaller eigenvalue. While the equation for the projection of the “phase space” distribution function onto the x - or y -directions is not as simple as that for $W_n(x)$ given above, it is not difficult to write a computer program which shows the values of these projections after a few time steps, starting with some initial distribution on the unit torus. Figures 3 and 4 show the behavior of the projected distribution functions, $W_n(x)$ and $G_n(y)$, onto the x - and y -directions, respectively, for an initial set of points that is uniform over the region $0 \leq x, y \leq 0.1$ and zero everywhere else. Both these distribution functions become uniform after three or four time steps. In Figs. 4 and 5, we show the evolution of the phase space distribution function

at some of the same times. Here we clearly see the difference on the rate of evolution of projected vs. full phase space distribution functions, and why, for simple models at least, the notions of ergodicity and mixing demand more than is physically required for an approach to equilibrium for the reduced distribution functions.

The important feature that both the baker’s map and the cat map have in common is that they are both area preserving maps with a stretching direction, or *unstable* direction, and a contracting direction, called a *stable* direction (Katok and Hasselblatt 1995). These directions are associated with *stretching* and *contracting* factors that depend exponentially upon time. The logarithms of these factors per unit time are the

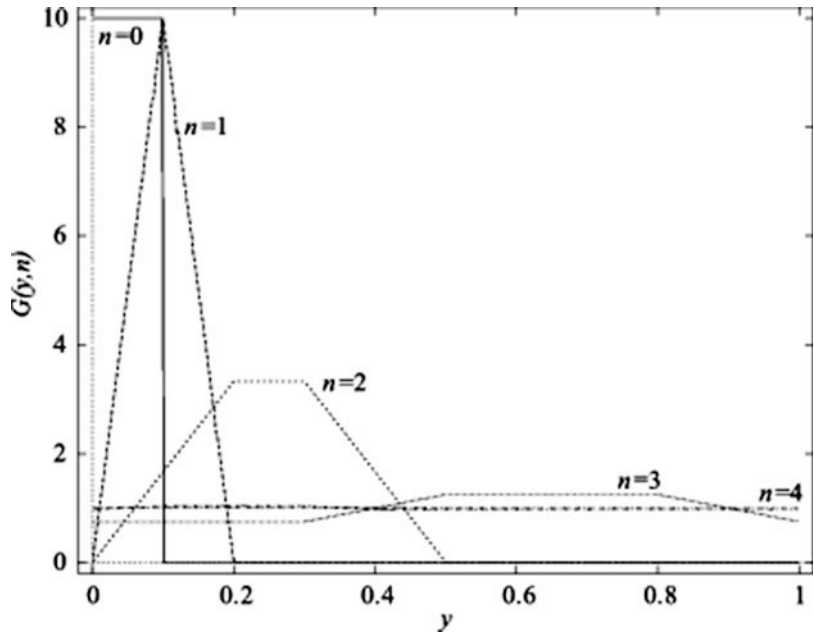
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Fig. 3 The projection of the Cat Map distribution onto the x -axis, $W_n(x)$, at various times, n . By $n = 3, 4$ the distribution is essentially uniform



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Fig. 4 The projection of the Cat Map distribution onto the y -axis, $G_n(y)$ at various times, n . By $n = 3, 4$ the distribution is essentially uniform

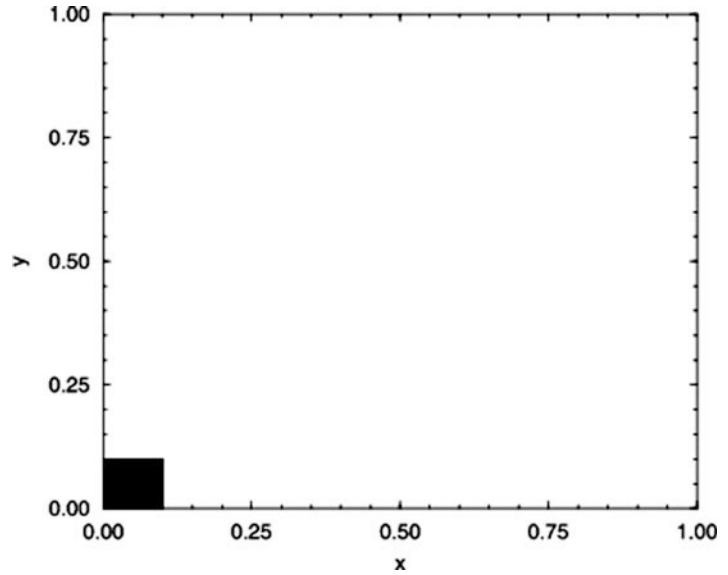


Lyapunov exponents (Eckmann and Ruelle 1985; Gaspard 1998; Katok and Hasselblatt 1995; Tél and Gruiz 2006). For the baker's map the two Lyapunov exponents are $\lambda_{\pm} = \pm \ln 2$, and for the cat map above, the two Lyapunov exponents are $\lambda_{\pm} = \ln [(3 \pm \sqrt{5})/2]$. In general, for higher dimensional systems, the stable and unstable directions span the so-called stable and unstable

manifolds, respectively. For the baker's map the y -axis and the x -axis are stable and unstable manifolds, respectively, for the baker's map, as are the axes in the eigen-directions of the cat map (Fig. 6). The importance of the unstable manifolds resides in the fact that on them non-uniform functions become smoothed with time, if they are not too singular, on a time scale that is determined by the

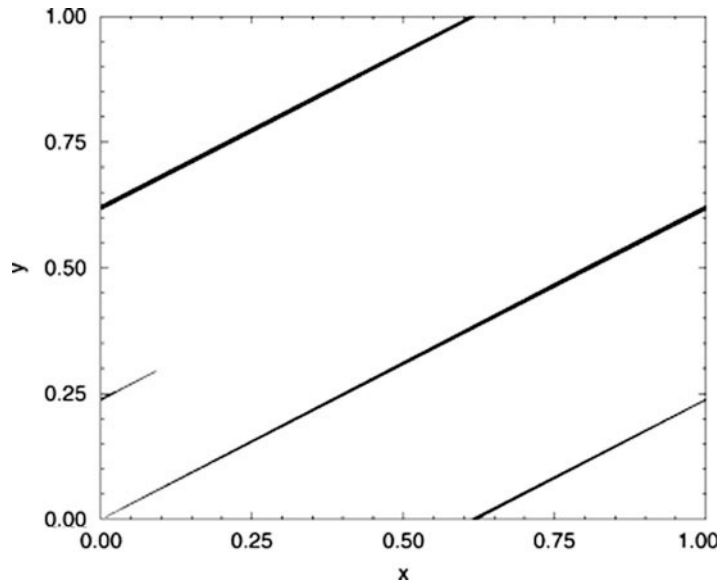
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Fig. 5 The initial phase space distribution used to obtain Figs. 3 and 4



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Fig. 6 The evolution of the phase space distribution of Fig. 5 after three iterations of the Arnold Cat Map



positive Lyapunov exponents. In order to get a reduced distribution function that approaches an equilibrium distribution for long enough times, one clearly must project the Liouville distribution onto manifolds that are not orthogonal to all of the unstable directions. This is one reason to examine the Cat Map, namely, to show that projections onto either direction, x or y equally lead to a uniform distribution after a few time steps. This would be the case for the baker's map, if we were

to project on any direction that makes a non-zero angle with the y -direction. Generally, the unstable directions in phase space are so complex that practically any projected distribution will not be orthogonal to them. Under time reversal the unstable and stable manifolds are interchanged, and the picture remains essentially the same. It is worth mentioning that if we were to project the distribution function onto a stable manifold we would not obtain an equilibrium distribution function, but

rather a very complicated function since any irregularities in the initial distribution function become more irregular with time, along stable directions (Gaspard 1997, 1998; Dorfman 1999; Tasaki et al. 1998). This is why a projection onto the y -axis would not lead to an equilibrium distribution for the baker's map, without some sort of coarse graining to "smooth out" an otherwise singular function.

Dynamical systems that have properties similar to the cat map or the baker's map are called *Anosov* or *Anosov-like* systems, respectively (Gaspard 1998; Katok and Hasselblatt 1995; Gallavotti and Cohen 1995). *Anosov* systems are continuous dynamical systems such that at every point in phase space there are stable and unstable directions, with positive and negative Lyapunov exponents, respectively. There may also be some *neutral* directions with zero Lyapunov exponents, but there must be at least one positive Lyapunov exponent. The presence of positive Lyapunov exponents is characteristic of a *hyperbolic* system. Furthermore, there must be at least one trajectory in phase space that is dense, a requirement which is called *transitivity*. Systems of particles with some manageable singularities such as hard spheres are not strictly *Anosov* systems but are close enough to be considered *Anosov-like*. The Arnold Cat Map is an example of an *Anosov* system, while the baker's map is *Anosov-like*. Of course, in a multidimensional *Anosov* system, there are a number of stable and unstable directions, and all stable manifolds intersect all unstable manifolds transversally. Systems with at least one positive Lyapunov exponents are commonly referred to as being *chaotic*. We have chosen simple systems to illustrate the main ideas, but the reader should be aware that it is possible to define Lyapunov exponents for motion on invariant sets in phase space, even for sets of measure zero, such as periodic orbits, or as we discuss below, fractal repellers.

Returning to statistical mechanics, we see that the simple examples of the baker's map and the Cat Map give us some reason to believe that, for chaotic systems at least, reduced distribution functions will approach equilibrium values, or more precisely, local equilibrium values, on

reasonable time scales. This conclusion depends, of course, on the assumption that the underlying microscopic dynamics is of the *Anosov* or *Anosov-like* variety. It is therefore useful to assume that systems of large numbers of particles with short ranged interactions, of general interest for statistical mechanics, are ergodic, *Anosov-like* systems as far as their dynamical properties are concerned. This assumption has been made a central feature of the dynamical systems approach to non-equilibrium statistical mechanics by Gallavotti and Cohen (1995), who have called it *the chaotic hypothesis*. This hypothesis allows one to apply the results of chaotic dynamics, such as those discussed in the next section, to realistic systems. In actuality we know little a priori about the dynamics of such systems, such as their Lyapunov exponents, or the structure and properties of unstable and stable manifolds in phase space. Furthermore, due to the work of Turaev, Rom-Kedar, Donnay (Turaev and Rom-Kedar 1998; Donnay 1996), and others, we know that if the intermolecular potential is smooth, there may exist regions in phase space where the dynamics is not chaotic. For these systems, the chaotic hypothesis implies the additional statement that the total volume of the non-chaotic regions in phase space is small enough so that for determining the important averages, they can be ignored.

Fractal Dimensions

An important concept used in applications of dynamical systems theory to statistical mechanics, among many other applications, is the notion of *fractal dimensions*. As we will mention in the next section, for chaotic systems many of the connections between macroscopic transport coefficients and microscopic dynamical quantities such as Lyapunov exponents can be related to the dimensions of fractal structures that form in the phase spaces of non-equilibrium systems. Generally, but not exclusively, fractals are defined by the statement that their dimension is not an integer. However, this definition is complicated by the fact that there are many ways to define the dimension of a set, and some fractals may have a dimension that is an integer by some definition

and non-integer by others. Fractals that have a variety of different dimensions are referred to as *multifractals*. There are also other definitions of fractals based upon self-similarity at all scales, or upon differentiability and continuity properties. We refer to the literature for more details (Ott 2002).

In order to present one definition of the fractal dimension of a set, imagine that the set is embedded in a d -dimensional space. Cover the set with cubes of length ϵ on a side, each labeled by an index i and suppose that one needs at least $N(\epsilon)$ of these cubes for a full coverage. Suppose further that we have a way to assign a measure μ_i to each cube. We can suppose that the total measure is normalized to some constant, say unity,

$$\sum_1^{N(\epsilon)} \mu_i = 1. \quad (16)$$

The measure μ_i may be a normalized Lebesgue measure of the cube, or it may be the fraction of time that a typical trajectory on the fractal spends in cube i , for example. In terms of this measure we can define a dimension D_q that depends on a continuous variable q , as

$$D_q = \frac{-1}{1-q} \lim_{\epsilon \rightarrow 0} \frac{I(q, \epsilon)}{\ln \epsilon}, \quad (17)$$

where $I(q, \epsilon)$ is given by

$$I(q, \epsilon) = \sum_{i=1}^{N(\epsilon)} \mu_i^q. \quad (18)$$

In this construction the quantity, D_0 is called the *box-counting dimension*, D_1 is called the *information dimension*, and D_2 is called the *correlation dimension*. The dimension D_q is a monotonic non-decreasing function of q . Other dimensions frequently employed to characterize fractals include the *Hausdorff dimension*, and we refer to the literature for a careful definition and discussion of this and other dimensions. As an example of a fractal, consider the *middle third Cantor Set*. This set is constructed by taking a unit interval, discarding the middle third of it, then take each

of the two remaining pieces, discarding the middle third of each of them, and so on. It is easy to show that the dimensions, D_q , of the remaining set, are all equal to $\ln 2 / \ln 3$.

Applications of Dynamical Systems Theory to Non-equilibrium Statistical Mechanics

The connections between normal transport, random walk processes, and the generalized Einstein formulae have allowed results from dynamical systems theory to be applied to non-equilibrium statistical mechanics in a direct way, at least for chaotic systems. However, one must study transport processes in a way that takes advantage of the fundamental properties of chaotic dynamics. Among the useful properties of chaotic systems are the formation of fractal structures in phase space. If the phase space is of sufficiently low dimensions then the fractal structures can be studied both by analytical methods and by computer simulated molecular dynamics. In addition to providing some insights into the approach to equilibrium for large systems, the dynamical systems approach gives us deep results of a more practical sort. Among these results are: (i) relations between transport coefficients and dynamical quantities, such as Lyapunov exponents and Kolmogorov-Sinai entropies, to be defined later in this chapter (Evans and Morriss 1990; Gaspard 1992a, 1998; Hoover 1999; Dorfman 1999; Ruelle 1999; Klages 2007; Ott 2002; Gaspard and Nicolis 1990; Dorfman and Gaspard 1995; Gaspard and Dorfman 1995); (ii) a theory of entropy production in non-equilibrium steady states and in the approach of a system to equilibrium (Evans and Morriss 1990; Gaspard 1997, 1998, 2004, 2006; Hoover 1999; Dorfman 1999; Ruelle 1999; Gallavotti 1999; Evans et al. 1993; Evans and Searles 2002; Gallavotti and Cohen 1995; Crooks 1999; Hoover and Posch 1994; Dorfman et al. 2002; Tél and Vollmer 2000; Vollmer 2002); and (iii) a number of fluctuation theorems – Evans-Searles-Gallavotti-Cohen theorems – which describe fluctuations in entropy production in non-equilibrium steady states

(Evans et al. 1993; Evans and Searles 2002; Gallavotti and Cohen 1995; Lebowitz and Spohn 1999; Crooks 1999; Kurchan 1998; Gaspard 2006; van Zon and Cohen 2004). Here we will summarize these results, and we refer the reader to the literature for a more complete discussion of these and related topics.

Microscopic Dynamical Quantities and Macroscopic Transport Coefficients

Among the many reasons dynamical systems theory attracted the attention of workers in non-equilibrium statistical mechanics were the connections between macroscopic transport coefficients of a system of particles and quantities that characterize the system's chaotic behavior discovered by Gaspard and Nicolis (Gaspard 1998, 1992a; Dorfman 1999; Gaspard and Nicolis 1990; Dorfman and Gaspard 1995; Gaspard and Dorfman 1995; Viscardi and Gaspard 2003), for Hamiltonian systems, and by Evans, Morriss, Hoover, Posch, and coworkers, for dissipative systems with Gaussian thermostats (Evans and Morriss 1990; Hoover 1999; Ruelle 1999; Klages 2007; Evans et al. 1990; Hoover and Posch 1994). We discuss each case separately.

The Escape-Rate Formulae for Transport Coefficients

Previously we noted that the Helfand moments related to transport undergo a random walk motion in phase space. Gaspard and Nicolis pointed out that if one considers a random walk in a space with *absorbing* boundaries one can combine results from random walk theory and from dynamical systems theory to obtain very interesting previously unknown connections between transport coefficients and quantities that characterize the microscopic chaotic dynamics.

The random walk theory that one needs for this connection is based on a Fokker-Planck equation for the probability distribution of the Helfand moments, $P(M_\sigma, t)$, where M_σ is a Helfand moment. We assume that the transport process is normal, that is, that the mean square fluctuations of the Helfand moment grows linearly with time. In such a situation the Fokker-Planck equation takes the simple form of a diffusion equation:

$$\frac{\partial P(M_\sigma, t)}{\partial t} = \alpha \frac{\partial^2 P(M_\sigma, t)}{\partial M_\sigma^2} \quad (19)$$

Here α is a constant proportional to the transport coefficient σ . Suppose now that we solve this diffusion equation in M -space with boundary conditions that when M_σ reaches the values $\pm\chi/2$, $P(M_\sigma, t) = 0$. That is, the Helfand moments undergo a Brownian motion in a space with absorbing boundaries such that the probability distribution vanishes whenever $|M_\sigma|$ reaches a specific value for the first time. Under these conditions, the probability distribution will decay exponentially, with a decay rate γ given by

$$\gamma = \alpha \left(\frac{\pi}{\chi} \right)^2. \quad (20)$$

A remarkable result from dynamical systems theory is that for chaotic systems, another expression holds for the same escape rate in terms of Lyapunov exponents and a quantity called the Kolmogorov-Sinai entropy per unit time (Gaspard 1993, 1998; Katok and Hasselblatt 1995; Gaspard and Rice 1989). This microscopic escape-rate formula for the escape-rate, γ_{mic} is

$$\gamma_{\text{mic}} = \sum_i \lambda_i^+(\mathcal{R}) - h_{\text{KS}}(\mathcal{R}). \quad (21)$$

All of the terms on the right hand side of Eq. (21) require some explanation. To get some insight into this formula, we now consider the microscopic dynamics of the system of particles and imagine that there is a set of initial conditions for all the particles for which the Helfand moment is in the region $-\chi/2 < M_\sigma < \chi/2$, and such that as the initial system evolves in time, either forward or backward, the Helfand moment will never reach the boundary. The set of all such initial conditions is called a *repeller* and denoted by $\mathcal{R}$. It is typically a fractal set of points in phase space, usually of measure zero in the set of all initial phase points, and a highly unstable set since an arbitrarily small displacement of the initial phase of the system from a point in $\mathcal{R}$ will lead to escape, unless the new initial point is also on the

repeller. Now imagine that we consider an infinitesimally small set of points in $\mathcal{R}$, and observe how these points separate in phase space in the course of time. If the dynamics on $\mathcal{R}$ is Anosov-like, there will be a set of positive Lyapunov exponents which we have denoted by $\lambda_i^+(\mathcal{R})$ in Eq. (21). The positive Lyapunov exponents on the repeller describe the rate with which trajectories on the repeller move apart. The other term in the escape-rate formula, $h_{\text{KS}}(\mathcal{R})$, is the Kolmogorov-Sinai entropy per unit time of the trajectories on $\mathcal{R}$, and can be understood in the following way. In general, dynamic entropies characterize the rate at which information about the exact trajectory of a system is gained or lost in the course of time. For example, if we know that the initial phase of a system is within some small region of phase space, then the *stretching* of the small region with time due to the dynamical instability allows us to locate the initial location of the trajectory ever more precisely as we follow the motion of the small initial set. If the system is closed, that is, there is no possibility of escape, then the amount of information about the initial location of the trajectory grows exponentially as the sum of the positive exponents. This result is known as Pesin's theorem. On the other hand, if the system is open and there is a possibility of escape, then the escaping trajectories lead to a loss of information (Dorfman and van Beijeren 1997). Hence a better way to write Eq. (21) is

$$h_{\text{KS}}(\mathcal{R}) = \sum_i \lambda_i^+(\mathcal{R}) - \gamma_{\text{mic}}. \quad (22)$$

In any case we now have two expressions for the same escape-rate for a hyperbolic system, and by equating them, we obtain an expression for the transport coefficient in terms of microscopic dynamical quantities, as

$$\alpha = \lim_{\chi \rightarrow \infty} \frac{\chi^2}{\pi^2} \left[\sum_i \lambda_i^+(\mathcal{R}) - h_{\text{KS}}(\mathcal{R}) \right]. \quad (23)$$

We have taken the large system limit to remove any possible dependence of the right hand side of Eq. (23) on the shape of the boundaries or on the

size of the system. This result is due to Gaspard and Nicolis (1990).

For two dimensional systems, one can reformulate the escape rate formula in terms of the information dimension, d_1 , of the repeller along the unstable direction (Gaspard 1998; Tél et al. 1996), which is given by $d_1 = h_{\text{KS}}/\lambda^+$, so that $\gamma = \lambda^+(1 - d_1)$.

The escape-rate formula has been used in molecular dynamics studies to obtain values for transport coefficients in a number of cases such as diffusion coefficients in periodic Lorentz gases, viscosities of simple systems and chemical reaction rates (Gaspard and Baras 1995; Viscardy and Gaspard 2003; Claus and Gaspard 2000; Claus et al. 2004; Bunimovich and Demers 2005). The results for the transport coefficients obtained by using the escape-rate methods agree with those obtained by other methods, often based on the Green-Kubo time correlation method, or, as discussed below, on Gaussian thermostat methods. There are as yet very few theoretical methods to compute the Kolmogorov-Sinai entropy for the repeller (Gaspard and Baras 1995; Gaspard 1998; Viscardy and Gaspard 2003), while both the transport coefficients, and, as it turns out, the sum of the positive Lyapunov exponents on the repeller are sometimes amenable to treatment by the usual methods of statistical mechanics and kinetic theory (van Beijeren and Dorfman 1995, 2001; van Zon et al. 2000).

Transport Coefficients and Phase-Space

Contraction in Gaussian Thermostatted Systems

An alternative method for relating macroscopic transport coefficients to Lyapunov exponents was developed by Evans, Hoover, Posch, and co-workers in their work on developing computer algorithms to simulate non-equilibrium flows in many-particle systems (Evans and Morriss 1990; Hoover 1999; Ruelle 1999; Evans et al. 1983, 1990, 2000; Hoover and Posch 1994; Posch and Hoover 1988, 1989; Chernov et al. 1993; Baranyi et al. 1993; Dellago et al. 1995, 1996; Dettmann 2000; Posch and Hirshl 2000). A problem arose in these simulations because the systems tended to heat up considerably due to the presence of viscous friction or, for charged particle systems, ohmic

heating. To counteract this heating, these authors introduced a fictitious thermostat which maintains a constant value for either the total energy or the total kinetic energy of the system. The thermostat was introduced by a modification of the equations of motion by the addition of a frictional force in such a way that the Hamiltonian nature of the system, in the usual coordinate, momentum, and time variables, is lost. This kind of frictional force was first introduced by Gauss in his study of mechanical systems with various constraints.

For systems with Gaussian thermostats, Liouville's theorem, which states that the phase space density at a point moving under the equations of motion does not change with time, is no longer satisfied. It is replaced by a conservation equation that relates the time derivative of the distribution function to the parameters characterizing the frictional forces. As a consequence, phase space volumes for thermostatted systems do not remain constant in time, but rather, on the average the phase space volume of a set decreases with time, the system approaches a *non-equilibrium* stationary state, and the system's distribution function approaches a distribution with fractal properties. The average rate of decrease of the phase space volume is given by a negative value of the sum of all of the Lyapunov exponents of the system. The non-equilibrium stationary state distribution is characterized by a special type of measure, called a Sinai-Ruelle-Bowen (SRB) measure, which describes the probability of finding a system in different regions of phase space. The SRB measure is characterized by the fact that it is smooth in the unstable directions in phase space but typically is fractal in the stable directions (Katok and Hasselblatt 1995). Simple examples of this type of measure can be found in the literature (Tasaki et al. 1998). The resulting fractal is called an *attractor*.

It is important to note that the decrease of the phase space volume and the concomitant formation of an attractor with a non-trivial SRB measure, does not mean that the fractal has zero dimension. Indeed, due to the decrease in phase space volume the *Lebesgue measure* of the phase space region where the trajectories are located approaches zero. However, the dimension of the resulting fractal is not zero. The box counting

dimension, D_0 , of the fractal may even coincide with the dimension of phase space, and the information dimension, D_1 , can often be expressed in terms of the Lyapunov exponents. For example for two-dimensional, thermostatted systems, with one positive Lyapunov exponent, λ^+ and one negative exponent, $-\lambda^-$, with $\lambda^+ - \lambda^- < 0$, the information dimension of the attractor is given by the *Kaplan-Yorke-Young formula* (Eckmann and Ruelle 1985; Ott 2002; Chernov et al. 1993; Evans et al. 2000) for two dimensional ergodic systems, as $D_1 = 1 + \lambda^+ / |\lambda^-|$.

The decrease of the phase space volume can also be related to the entropy production in the system+thermostat. This entropy production can also be related to the transport coefficients via the usual macroscopic laws of irreversible thermodynamics. Thus, one has a way to relate transport coefficients to the sum of the Lyapunov exponents for these thermostatted systems.

To make this discussion more concrete, we consider the example of a hard-ball Lorentz gas (Tél and Vollmer 2000; Chernov et al. 1993; Baranyi et al. 1993; Dettmann 2000; Posch and Hirshl 2000). We assume that the moving particles have a bounded free path between collisions with the fixed scatterers, and that the scatterers do not form traps without escape for the moving particles. We suppose the moving particles have mass, m , and carry a charge, q , (but still do not interact with each other) and are placed in a constant, external electric field, $\mathbf{E}$. Ordinarily, the field will accelerate the moving particles in such a way that their energy increases over time. To avoid this we add a frictional force to the equations of motion of the moving particle, and adjust the frictional force so as to keep the kinetic energy of the moving particle constant in time. The equations of motion for the position, $\mathbf{r}$ and velocity, $\mathbf{v}$, of the moving particle between collisions with scatterers are

$$\dot{\mathbf{r}} = \mathbf{v} \quad (24)$$

$$\dot{\mathbf{v}} = \frac{q\mathbf{E}}{m} - \alpha\mathbf{v}, \quad (25)$$

where α is a dynamical variable defined by the constant energy condition, $\dot{\mathbf{v}} \cdot \mathbf{v} = 0$. Thus we find that

$$\alpha = \frac{q\mathbf{v} \cdot \mathbf{E}}{mv^2}. \quad (26)$$

The equations of motion given above for the moving particle must be supplemented by the equations describing the collisions of the moving particles with the scatterers. To simplify matters, we will suppose that the particles make instantaneous, elastic, and specular collisions with the scatterers.

If we define the Gibbs entropy for this system in terms of the phase space distribution function, $\rho(\mathbf{r}, \mathbf{v}, t)$, by

$$S_G(t) = -k_B \int d\mathbf{r} \int d\mathbf{v} \rho(\mathbf{r}, \mathbf{v}, t) [\ln \rho(\mathbf{r}, \mathbf{v}, t) - 1], \quad (27)$$

where k_B is Boltzmann's constant, one finds that

$$\frac{dS_G}{dt} = -k_B \int d\mathbf{r} \int d\mathbf{v} \alpha \rho = -k_B \langle \alpha \rangle. \quad (28)$$

The average value is taken with respect to the phase space distribution function for the moving particles, ρ . This entropy actually decreases with time, since on the average α is positive. This decrease in entropy must be matched, at least, by an increase in entropy of the reservoir that is responsible for the additional frictional force. Thus

$$\frac{dS_{\text{reservoir}}}{dt} \geq k_B \langle \alpha \rangle \geq 0. \quad (29)$$

We now take the entropy production in the reservoir to be given by the usual macroscopic laws, in particular,

$$\frac{dS_{\text{reservoir}}}{dt} = \frac{\mathbf{J} \cdot \mathbf{E}}{T} = \frac{\sigma E^2}{T}, \quad (30)$$

where $\mathbf{J} = \sigma \mathbf{E}$ is the electrical current produced by the moving particles and σ is the coefficient of electrical conductivity. Then, by combining Eqs. (29) and (30), and assuming that we take the entropy production in the reservoir to be exactly $k_B \langle \alpha \rangle$, we obtain an expression for σ as

$$\sigma = \frac{k_B T \langle \alpha \rangle}{E^2}. \quad (31)$$

The final step in this process is to relate the average friction coefficient, $\langle \alpha \rangle$, to the Lyapunov exponents for the trajectories of the moving particles. We note, first of all, that the volume, $\mathcal{V}$ of a small region in phase space will change exponentially in time with an exponent equal to the sum of all the Lyapunov exponents, as

$$\mathcal{V}(t) = \mathcal{V}(0) \exp \sum_i \lambda_i, \quad (32)$$

since the Lyapunov exponents describe the rates of stretching or of contracting of small distances in phase space. A simple argument shows that

$$\left\langle \frac{d \ln \mathcal{V}}{dt} \right\rangle = -\langle \alpha \rangle = \left\langle \sum_i \lambda_i \right\rangle. \quad (33)$$

In the non-equilibrium stationary state, all averages remain constant with time, so that we can now use Eq. (31) to obtain the desired connection between a transport coefficient, in this case the conductivity σ , and the average Lyapunov exponents,

$$\sigma = -\frac{k_B T}{E^2} \left\langle \sum_i \lambda_i \right\rangle. \quad (34)$$

This result has been used to determine the conductivity and the diffusion coefficient of the moving particles in the Lorentz gas by means of efficient computer algorithms for determining the Lyapunov exponents (Baranyi et al. 1993; Dettmann 2000; Posch and Hirshl 2000). Similar methods have been used to determine the shear viscosity (Evans et al. 1990) and other transport properties of systems with short range, repulsive potentials.

One important result of the analysis of these thermostatted systems is the *conjugate pairing rule*. This is a generalization of the result for chaotic Hamiltonian systems that non-zero Lyapunov exponents come in pairs, with the same magnitude but with opposite signs so that members of each conjugate pair sum to zero

(Ott 2002). This is called the *symplectic conjugate pairing rule*. For many chaotic systems with Gaussian thermostats it is possible to prove another conjugate pairing rule where the Lyapunov exponents form conjugate pairs which sum to a non-zero value, independent of which pair of exponents is chosen (Evans et al. 1990; Dettmann and Morriss 1996; Wojtkowski and Liverani 1998). The conjugate pairing rule is very helpful for analyzing relations such as that given by Eq. (34), since the right hand side is completely determined by the sum of any one conjugate pair of exponents. The easiest pair to use is the pair formed by the positive and negative exponents with the largest magnitude.

Ruelle-Pollicott Resonances and Irreversible Processes

For a Hamiltonian N -particle system, the phase space distribution function, $\rho(\Gamma, t)$ evolves in time according to the relation given by the Liouville equation, in terms of a time evolution operator, $\mathcal{S}(-t)$, as

$$\begin{aligned}\rho(\Gamma, t) &= \mathcal{S}(-t)\rho(\Gamma, 0) \\ &= \exp -t\mathcal{L}\rho(\Gamma, 0) \\ &= \rho(\Gamma(-t), 0),\end{aligned}\quad (35)$$

where we indicate that the phase space variables Γ evolve as

$$\Gamma(t) = \mathcal{S}(t)\Gamma = \exp t\mathcal{L}\Gamma. \quad (36)$$

Here $\mathcal{L}$ is the Liouville operator, when acting on differentiable functions, is given, for an isolated system of N particles, by

$$\mathcal{L} = \sum_{i=1}^N \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} + \sum_i \mathbf{F}_i \cdot \frac{\partial}{\partial \mathbf{p}_i}, \quad (37)$$

where $\mathbf{F}_i$ is the total force on particle i due to the other particles, and external sources such as walls of a container.

If one insists that the functions on which the time displacement operator acts be ordinary functions with well-behaved derivatives, the exponential operators, $\mathcal{S}$ appearing in Eqs. (35), (36) are

unitary with spectrum on the unit circle. In view of this observation it is difficult to see how a satisfactory theory of irreversible behavior, including decays in time, might be obtained from such an operator. The answer is to be found by enlarging the space of functions to include singular functions such as Schwartz distributions (Gaspard 1998). The discussion in the previous subsection has indicated that distributions may evolve to fractals, which are typically non-differentiable functions, so it is very natural to include singular functions in the space of functions on which the time evolution operator may act. In this enlarged function space, the time evolution operator may have properties that do not obtain in a more restricted space of functions. Under these circumstances one studies the right and left eigenfunctions of the Liouville operator, $\mathcal{L}$ in a structure called a *Gelfand triplet* or *rigged Hilbert space* (Bohm and Gadella 1990). There are two sets of such triplets corresponding to forward and time reversed motion.

A Gelfand triplet is an operator, together with the two spaces spanned by its right and left eigenfunctions, and an inner product involving one function from each of the two spaces. If the right eigenfunctions are singular functions, the left eigenfunctions must be sufficiently well behaved so that the inner product of a function in the “singular” space with a function in the “smooth” space is well defined. The eigenvalues for the time displacement operator appear as two different sets of poles of the resolvent operator, $(z - \mathcal{L})^{-1}$, in the complex plane, one for forward and one for time-reversed motion. The poles are called *Ruelle-Pollicott resonances* (Pollicott 1985, 1986; Ruelle 1986a, b), and they give the relaxation rates for various processes that can take place in the system. The time reversal symmetry of the motion provides the relation between the two sets of resonances in the complex plane. For simple models it is possible to construct the functions, singular and smooth, in a Gelfand triplet and to locate the resonances in the complex plane (Dörflé 1985; Gaspard 1992b, c). In addition to poles of the resolvent one may, in general, expect to find branch cuts, etc. in the complex plane (Gaspard 1998). The existence of these resonances provides

an argument that the rates of relaxation to equilibrium found by using traditional methods of statistical mechanics, including kinetic theory, are not artifacts of the approximations made in arriving at these results, but are reflections of the existence of Ruelle-Pollicott resonances for the system.

Fractal Forms in Diffusion and a Dimension Formula

For chaotic systems, the relation between the mean square displacement of a diffusing particle and the diffusion coefficient conceals a fractal function. This can be understood on the basis of the following observation: Since the actual displacement of the diffusing particle depends on the initial phases of the particles in the system, even the slightest change in these phases will make a large change in the displacement of the Brownian particle. One way to try to capture some features of this variation of the displacement is to consider simple models of diffusion that are deterministic, chaotic, and diffusive (Fox 1997; Gaspard 1996). The process of diffusion in these models is often referred to as deterministic diffusion, since no stochastic elements are introduced in the dynamics of the models. Here we illustrate this idea using the two dimensional periodic Lorentz gas with finite free paths of the moving particle between collisions, so that diffusion is well

defined in this system (Fox 1997; Gaspard 1996; Gilbert et al. 2001) (Fig. 7).

It is very convenient to use the van Hove intermediate scattering function as a way of describing the diffusive process. This function, denoted by $F_k(t)$, is defined as

$$F_k(t) = \left\langle e^{[ik \cdot (r(t) - r(0))]} \right\rangle, \quad (38)$$

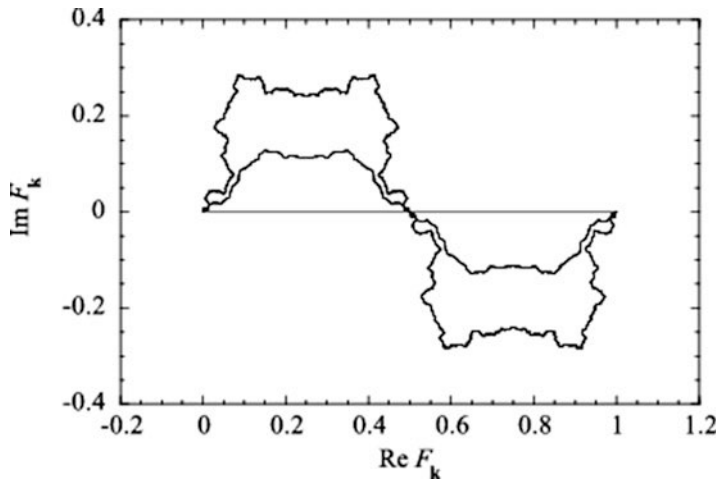
where the average is taken over an equilibrium ensemble. The van Hove function is related to the probability of finding the diffusing particle at point r at time t , $P(r, t)$ by

$$P(r, t) = \int \frac{dk}{(2\pi)^d} P_k F_k(t), \quad (39)$$

where d is the number of spatial dimensions of the system and P_k is the Fourier transform of the initial probability distribution for the diffusing particle. One can use a cumulant expansion in the exponent to show that $F_k(t)$ is given by

$$F_k(t) = e^{s(k)t}, \quad (40)$$

where $s(k)$ is the wave-number dependent decay rate for diffusive motion. Thus, for wave numbers,



Chaotic Dynamics in Nonequilibrium Statistical Mechanics, Fig. 7 The incomplete van Hove function for a periodic Lorentz gas where a point particle of unit mass and velocity undergoes elastic collisions with hard disks of unit radius forming a triangular lattice with

interdisk distance $d = 2.3$: Curves of the cumulative functions for wavenumber $k_x = 0.0, 0.5$, and 0.9 with $k_y = 0$. Note that the fractality increases with the wavenumber

k much smaller than the inverse of a lattice spacing, in this case, unity, this function takes the form

$$s(k) = -Dk^2 + \tilde{D}k^4 + O(k^6), \quad (41)$$

where D is the diffusion coefficient, $\tilde{D}$ is called the super-Burnett diffusion coefficient, etc. In order to see the physics that is obscured by taking the equilibrium average, consider the microscopic quantity that is averaged, namely, $\exp[i\mathbf{k} \cdot (\mathbf{r}(t) - \mathbf{r}(0))]$. If the motion of the particle is chaotic, the displacement over a time t is a very rapidly varying function of the initial point $\mathbf{r}(0)$. As a result, the exponential containing this displacement will be a rapidly oscillating function of the initial point. To capture these oscillations and to explore the fractal structure of the exponential function, we consider a partially averaged quantity, which we will call a normalized, incomplete van Hove function, $F_k(\theta, t)$, defined by

$$F_k(\theta, t) = \frac{\int_0^\theta d\theta' e^{[i\mathbf{k} \cdot (\mathbf{r}(\theta', t) - \mathbf{r}(\theta', 0))]} }{\int_0^{2\pi} d\theta' e^{[i\mathbf{k} \cdot (\mathbf{r}(\theta', t) - \mathbf{r}(\theta', 0))]} }. \quad (42)$$

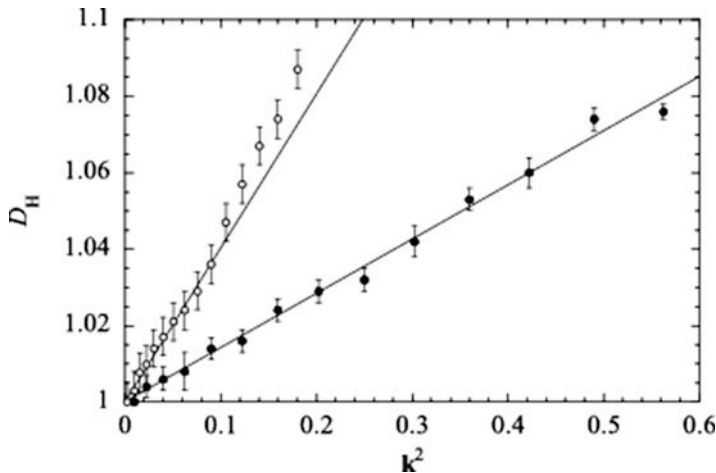
Here we take initial points to be uniformly distributed just outside the surface of one of the scatterers in the periodic Lorentz gas, with initial

velocity directed radially outward. The point on the surface is indicated by the angle θ taken with respect to some fixed direction. If one waits for a sufficient number of collisions to take place so that the motion is diffusive, and then plots $\text{Im } F_k(\theta, t)$ vs $\text{Re } F_k(\theta, t)$ one finds a fractal curve for small values of the wave number, $|k|$. Computer results obtained by Claus et al. (Gaspard et al. 2001) for the hard disk Lorentz gas are plotted in Fig. 7 for various values of the wave number.

It is possible to prove that there exists a striking connection between the fractal Hausdorff dimension, $\mathcal{D}_H$, of the curve $(\text{Re } F_k(x), \text{Im } F_k(x))$, for the incomplete van Hove function (Gaspard 1996; Gilbert et al. 2001), for small k , the diffusion coefficient, D , and the positive Lyapunov exponent, λ , characterizing the chaotic process underlying the diffusive motion of the particle. This connection is illustrated in Fig. 8 and given by the equation

$$\mathcal{D}_H(k) = 1 + \frac{D}{\lambda} k^2 + O(k^4). \quad (43)$$

Also illustrated in Fig. 8 is the analogous curve obtained from the incomplete van Hove function



Chaotic Dynamics in Nonequilibrium Statistical Mechanics, Fig. 8 Hausdorff dimension $\mathcal{D}_H$ of the incomplete van Hove function versus $k^2 = k_x^2$ ($k_y = 0$) for both periodic Lorentz gases with hard-disk scatterers (filled circles) and for the case where the hard disks are replaced by repulsive Coulomb scatterers on a square

lattice, and the energy of the particle is sufficiently high for the motion to be chaotic (open circles). Both solid lines have slopes equal to $\mathcal{D}/\lambda$ for the respective diffusion coefficient $\mathcal{D}$ and Lyapunov exponent λ of the Lorentz gases

when the hard disk potential is replaced by a repulsive Coulomb potential. For sufficiently high energy of the moving particle, the motion of the moving particle is chaotic and the van Hove function also shows fractal properties. Thus the fractal curves are not artifacts of the hard disk potential. Equation (43) illustrates the fact that for chaotic models such as the one discussed here, the incomplete van Hove function encodes in its structure both a macroscopic property of the system, the diffusion coefficient, and a microscopic property, the Lyapunov exponent. Such interesting connections are central to a deeper understanding of the microscopic foundations of transport processes.

Entropy Production in Non-equilibrium, Hamiltonian Systems

One of the subjects of most active research in recent years has been the theory of entropy production in non-equilibrium systems. Dynamical systems theory has provided some new insights into this old problem. Briefly formulated, the problem is to explain the positive, irreversible production of entropy using the fundamental ideas in statistical mechanics, particularly the Liouville equation. The obstacle in this direction that must be overcome somehow is the fact that the Gibbs entropy

$$S_G(t) = -k_B \int d\Gamma \rho(\Gamma, t) [\ln \rho(\Gamma, t) - 1], \quad (44)$$

remains constant in time if $\rho(\Gamma, t)$ satisfies the Liouville equation for Hamiltonian systems

$$\frac{d\rho(\Gamma, t)}{dt} = 0. \quad (45)$$

Here Γ represents all of the coordinate and momentum variables of the system. The usual way around this difficulty is to introduce a coarse grained entropy, obtained by either defining an entropy in terms of reduced distribution functions, as is done in Boltzmann's famous H-theorem, or by coarse graining the phase space itself, and defining an entropy in terms of the average

phase space distribution in each of the coarse graining regions (Ruelle 1999). In either case, it is possible to show that the rate of production of the redefined entropy is positive, and for the Boltzmann case at least, is in agreement with the predictions of irreversible thermodynamics when the gas is close to a local equilibrium state.

Ideas from dynamical systems theory have not changed the fundamental need for coarse graining. Instead they have provided strong reasons for doing it, reasons that were lacking in the previous approaches, where the motivation for coarse graining seemed only to be that it was necessary to coarse grain in some way to get a positive entropy production. The central new idea in this area is that the phase space description of a non-equilibrium process requires, in the thermodynamic limit at least, the use of distribution functions that are defined on fractal sets. A simple example is provided by a system in which diffusion can take place in a region between two particle reservoirs, each reservoir being maintained at a different density of particles (Gaspard 1997, 1998). Then if the dynamics that leads to transport of the particles between the reservoirs is Anosov-like, one can argue, and in simple enough cases show explicitly, that the regions in phase space that correspond to regions of different density in the system get so tangled up and enmeshed that the distribution function is a wildly varying fractal function. As such, it is no longer differentiable and the steps that lead to the proof of the constancy of the Gibbs entropy can no longer be justified. The only way to treat this kind of fractal behavior of the distribution function is to smooth the function in one or another way, typically by defining cumulative distribution functions over small regions of phase space, leading to the construction of SRB measures. In simple cases, one can show that fractal forms appear in the phase space distribution function for systems in non-equilibrium stationary states produced by particle reservoirs, or in the relaxation of a system with particle diffusion to equilibrium, and that the rate of entropy production agrees with the predictions of irreversible thermodynamics (Gaspard 1997, 1998; Dorfman et al. 2002; Fox

1998; Goldstein et al. 1998). However, much needs to be done to extend this work to other hydrodynamic processes and to understand why the results of macroscopic theory are obtained in this way. Recently, Gaspard has presented an expression for the rate of entropy production in chaotic as well as in stochastic systems as the difference in two dynamical entropies per unit time, one a form of the Kolmogorov-Sinai entropy per unit time, and the other, an entropy per unit time for the time reversed motion but as measured by the measure of the forward process. It is possible to prove that this rate of entropy production is positive, and for the cases studied so far, agrees with the results of irreversible thermodynamics (Gaspard 2004, 2006).

Kinetic Theory Methods for Analytical Calculations of Lyapunov Spectra

As we demonstrated in the examples given above for the applications of chaos theory to non-equilibrium processes, an important role is played by Lyapunov exponents and Kolmogorov-Sinai entropies per unit time. Apart from computer simulations, it is not always clear how one might obtain expressions and values for these quantities. In some simple cases such as the baker's map and toral automorphisms, the calculation of the Lyapunov exponents is a simple matter. However these cases are very special and rarely are realistic models for physical systems. Thus the problem remains of finding general methods for an analytic determination of Lyapunov exponents and Kolmogorov-Sinai entropies. One such method is kinetic theory. Using the Boltzmann and related equations (Dorfman 1999; Chapman and Cowling 1970), van Beijeren and coworkers have been able to obtain expressions for Lyapunov exponents, and in some cases, Kolmogorov-Sinai entropies, for dilute gases with short range potentials, such as hard ball systems, and for dilute Lorentz gases (Dorfman 1999; van Beijeren and Dorfman 1995, 2001; van Zon et al. 1998, 2000; de Wijn and van Beijeren 2004). Results obtained this way are in good agreement with the results of computer simulations. We refer to the literature for details.

Entropy Production in Systems with Gaussian Thermostats and the Cohen-Gallavotti Fluctuation Theorem

As a final example of the applications of dynamical systems theory to non-equilibrium statistical mechanics we briefly discuss one example of a number of closely related fluctuation theorems, first obtained by Evans, Searles, and by Gallavotti, and Cohen, and generalized by Spohn and Lebowitz, among others (Evans et al. 1993; Evans and Searles 2002; Gallavotti and Cohen 1995; Lebowitz and Spohn 1999; Crooks 1999; Kurchan 1998). These fluctuation theorems are very closely related to a class of work-free energy fluctuation results due to Jarzynski (1997), and Crooks (1999), as well as to the expression for entropy production given by Gaspard (2004, 2006), as mentioned above. By now the literature is quite extensive and the reader is directed there for more details. Here we discuss, briefly, the Gallavotti-Cohen version of a fluctuation theorem appropriate for systems with Gaussian thermostats (Gallavotti and Cohen 1995). In the discussion of systems with energy conserving thermostats, we have introduced another idea for entropy production, namely, entropy production in a reservoir associated with phase space contraction of a thermostatted system. Here the central idea is that the thermostatted dynamics produces an attractor for the system's trajectories in phase space. The friction coefficient, which we have denoted by α , is a dynamical function taking on positive or negative values depending on the trajectory of the system in phase space. To produce an overall phase space contraction, the friction coefficient should be positive on average, but from time to time it may be negative. Loosely speaking, we might say that the entropy production in the system is positive when the value of α is positive at the time, and negative when α is negative. For example, in the Lorentz gas that we have been discussing, when the particle moves in the direction of the field, α is positive, and when it moves opposite to the direction of the field, α is negative, provided the charge q is positive. One might imagine some time interval τ , say, and ask for the probability that the time-

averaged entropy production per unit time, ϵ_τ , as measured by the phase space contraction, has a value a over this time interval. This probability can be expressed in terms of the SRB measure on the attractor of the steady state system. The fluctuation theorem for this system is a result for the ratio of the probability that the time-average entropy production per unit time over an interval τ will be the value a , to the probability that this value will be $-a$. For a reversible, Anosov-like system with a Gaussian thermostat, the theorem is

$$\frac{\text{Prob}(\epsilon_\tau = a)}{\text{Prob}(\epsilon_\tau = -a)} = e^{a\tau} \quad (46)$$

Note that for long times this ratio approaches zero or infinity depending upon the sign of a .

This result was first discovered by means of computer simulations by Evans, Cohen, and Morriss (1993), and this observation was explained on the basis of Anosov-like dynamics by Gallavotti and Cohen (1995). A closely related fluctuation formula was derived by Evans and Searles (2002). By now this class of fluctuation theorems has been generalized considerably to include analogous results for stochastic and other kinds of systems. We refer to the literature mentioned above for further details.

Discussion

Here we described some aspects of the theory of irreversible processes, as seen from the point of view of dynamical systems theory. We described the notions of ergodic and mixing properties of a dynamical system and argued that they alone are insufficient for a full explanation of the approach to equilibrium as seen on laboratory time scales. However, we tried to argue that if the microscopic system has positive Lyapunov exponents connected to unstable manifolds in the phase space, then one can argue that an approach to equilibrium of reduced distribution functions can occur on much shorter times scales than those needed to establish the mixing of phase space regions throughout the entire phase space. Moreover the existence of a chaotic microscopic

dynamics allows us to derive some very striking connections between macroscopic transport coefficients and quantities such as Lyapunov exponents, fractal dimensions, Kolmogorov-Sinai entropies, that characterize the underlying chaotic, microscopic dynamics of the system. Much, but not all, of our discussion was based on some very simple examples of classical chaotic systems with few degrees of freedom, the baker's map and the Arnold Cat Map. These are simple Anosov-like and Anosov systems where one can analyze many points in some detail. However, this analysis is still very far from an analysis of systems of real interest to statistical mechanics, where the number of degrees of freedom is generally much, much larger, even for systems of particles studied on computers, and where the dynamics is not always chaotic. Therefore, it is very much an open question to show that this picture persists when the systems studied are of macroscopic size, and the dynamics is treated in a more realistic way.

Finally we should say something about the role that quantum mechanics plays in our understanding of the approach of a system to equilibrium. "Quantum chaos" is a subject that has developed an enormous literature (Srednicki 1999; Haake 2001; Stöckmann 1999; Wojcik 2006), primarily associated with the quantum behavior of systems with few degrees of freedom which are chaotic in the classical limit of $\hbar \rightarrow 0$. This work is clearly of great importance for understanding the behavior of *mesoscopic* quantum devices such as quantum dots and related materials. However, there is no analog of dynamical chaos in quantum mechanics and no direct translation of the results described here to quantum systems. This is a result of the fact that the limit as $\hbar$ approaches zero *does not commute* with the limit of t approaching infinity. Therefore one cannot typically study the asymptotically long time behavior of a quantum system whose classical counterpart is chaotic, and then by taking the limit of $\hbar$ approaching zero, obtain the correct, chaotic behavior of the classical system. Instead one may look for some sign in the quantum motion that the classical system is chaotic. Typically a quantum system will exhibit some signs of the chaotic behavior of the classical system in the semi-classical region of small, but

not zero $\hbar$, for some period of time known as the *Ehrenfest time*. The Ehrenfest time is essentially the time that it takes an initially small wave packet to expand to some characteristic length in the system. While the packet is small, the semi-classical behavior is essentially that of a classical system. The rate of the expansion of the wave packet is determined by the classical Lyapunov exponents. When the wave packet reaches a certain size, then the motion of the system is governed by interference and diffraction effects that have no classical counterpart. For example, while a classical particle moving among a random array of fixed scatterers exhibits normal diffusion, its quantum counterpart can be localized, or move diffusively, depending upon the spatial dimension of the system and the particle's energy.

The comments above suggest that chaotic dynamics has a large role to play in quantum systems when one looks at the semi-classical regime, namely, the regime where $\hbar$, in proper dimensionless units, can be considered very small (Haake 2001; Stöckmann 1999). One important result, known as *Schnirelman's Theorem* (Lazutkin 1993) states that in the semi-classical limit, most of the wave functions for a quantum system, whose classical counterpart is chaotic and ergodic, become "equidistributed" on the constant energy surface. This means that the probability of finding the system in some region becomes equal to the ratio of the measure of that region to the total measure of the region available to the system. Nevertheless, there are some wavefunctions for classically chaotic systems that exhibit *scars* in the semi-classical limit, where the wave function is concentrated on periodic orbits of the classical motion. The scarred wave functions then form a special class which do not satisfy Schnirelman's Theorem. In this connection we also mention *Berry's conjecture* (Berry 1977) which states that the high energy wavefunctions for a classically chaotic, ergodic system can be represented as a Gaussian random function, such as a superposition of plane waves with random phases. For further details we refer to the literature listed above.

The understanding of the approach to equilibrium in macroscopic systems typically requires a

treatment of quantum systems with a very large number of degrees of freedom. Such systems are not likely to be in one or in a superposition of a few energy eigenstates. Instead, such systems are likely to be in a state that is a superposition of a huge number of such quantum states, and destructive interference of the phase relations among the states is an important ingredient of the behavior of such systems (van Kampen 1988). In fact there is a large literature that deals with the phenomenon of the loss of coherence, or *decoherence*, of superpositions of large numbers of quantum states for a macroscopic system, and helps us understand a bit more clearly why classical mechanics is a good approximation for describing systems that we know to be intrinsically quantum mechanical.

Future Directions

We conclude with a list of open questions that will provide some indication of what directions might be fruitful for further work in the future. This list is far from exhaustive, but focuses upon the particular issues addressed here.

1. Most of the results described here that connect microscopic dynamics and macroscopic transport, such as the escape rate formulae, Eq. (23), the dimension formula Eq. (43), and the Lyapunov exponents-transport coefficient relations for Gaussian thermostatted systems Eq. (34), have been proven for purely chaotic, Anosov or Anosov-like systems, only. The phase spaces of most realistic systems are not likely to be purely chaotic. Instead one expects realistic systems to have mixed phase spaces with both chaotic regions and non-chaotic regions. So far a satisfactory treatment of transport in mixed systems is in a very rudimentary shape, except for some models which have been studied extensively. It would be useful to have estimates of the size and importance of non-chaotic regions in many-particle systems and to determine what corrections, if any, are needed to generalize the results mentioned above to mixed systems.

2. Most of the results given here have been illustrated, and in some cases only derived, for low dimensional systems. How much of this discussion is relevant for systems with many particles where the dimension of phase space is very large? For example, the formula connecting diffusion and Lyapunov exponents, given by Eq. (43), has only been derived for diffusion in two dimensional chaotic systems Lorentz gases. What is the generalization of this formula to higher dimensions and to general transport processes?
3. The fact that our detailed understanding of the role of chaos in non-equilibrium processes is for systems of low dimensionality suggests that applications of chaos to nanoscale systems might be very fruitful (Gaspard 2006).
4. Pseudo-chaotic systems present a great challenge both to physicists and to mathematicians (Gutkin 1996; Tabachnikov 2005). Are there general statements one can make about the motion of a particle in a collection of scatterers, such as hard squares or other scatterers where the motion is not chaotic at all, and the rate of separation of trajectories is at best algebraic? How do these properties depend on the geometrical structure and arrangements of the scatterers? Are there generalizations of the escape-rate formula, and the others mentioned here, to pseudo-chaotic systems?
5. There are at least a few logical gaps in the applications of dynamical systems theory to non-equilibrium statistical mechanics. On one hand we have argued that as far as the approach to equilibrium is concerned it makes sense to look at projected distributions since these distribution functions reach equilibrium forms long before the full phase space distribution function does. This statement itself needs a careful proof for realistic systems. Moreover, the derivations of the formulae that connect transport properties with microscopic dynamical quantities rely upon the use of the full phase space. This suggests that there is a fundamental issue of relevant time scales that needs to be resolved, in order to determine the time scales on which these results become valid.

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Monte Carlo Simulations in Statistical Physics

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Glossary

Classical statistical mechanics Statistical mechanics relates the macroscopic properties of matter to basic equations governing the motion of the (many!) constituents from which matter is built from. For classical statistical mechanics these equations are Newton's laws of classical mechanics.

Critical slowing down Divergence of the relaxation time of the model describing the dynamics of a many-particle system when one approaches a second-order phase transition (= "critical point" in the phase diagram).

Detailed balance principle Relation linking the transition probability for a move and the transition probability for the inverse move to the

ratio of the probability for the occurrence of these two states connected by these moves in thermal equilibrium.

Equilibrium Statistical mechanics considers "thermal equilibrium," i.e., a many-body system in contact with a (big) heat reservoir does not take up heat from this reservoir, its macroscopic properties do not change with time, and a few global properties (like temperature, pressure, particle number) suffice to characterize the state of the system.

Ergodicity Property that ensures that ensemble averages of statistical mechanics (taken with the proper probability distribution) agree with time averages taken along the trajectory along which the system moves through its state space.

Finite-size scaling Theory that describes the rounding and shifting of singularities that thermodynamic properties exhibit when the state of a system changes from one phase to another in the "thermodynamic limit" (i.e., particle number $N \rightarrow \infty$).

Importance sampling Monte Carlo method that chooses the states that are generated according to the probability distribution that one desires to realize. For example, for statistical mechanics applications, states are chosen with weights proportional to the "Boltzmann factor" $\{\exp [-\text{energy of the state/temperature}]\}$.

Master equation Rate equation describing the "time" – evolution of the probability that a state occurs as a function of a "time" coordinate labeling the sequence of states.

Molecular dynamics method Simulation method for interacting many-body systems based on the numerical solution of Newton's equations of motion of classical mechanics.

Monte Carlo step Unit of (pseudo) time in (dynamically interpreted) importance sampling where, on the average, each degree of freedom in the system gets one chance to be changed (or "updated").

Quantum statistical mechanics Statistical mechanics relates the macroscopic properties

of matter to basic equations governing the motion of the (many!) constituents matter is built from. For quantum statistical mechanics, this basic equation is the Schrödinger equation for the many body wavefunction. If the eigenvalue spectrum of this equation could be obtained, the canonical formalism of statistical mechanics could be straightforwardly applied; since normally this is not possible, one has to use a reformulation of the Schroedinger equation in terms of path integrals.

Random number generator (RNG) Computer subroutine to produce pseudorandom numbers that are approximately uniformly distributed in the interval from zero to unity. Approximately the subsequently generated random numbers are uncorrelated. RNG's typically are deterministic algorithms and strictly periodic, but the period is large enough that for many applications this periodicity does not matter.

Simple sampling Monte Carlo method that chooses states uniformly and at random from the available space.

Thermodynamic variables Macroscopic pieces of matter (solids, liquids, gases) in thermal equilibrium can be characterized by a few state variables, "extensive" thermodynamic variables (proportional to the particle number, such as energy, volume) and "intensive" ones (independent of the particle number, such as temperature, pressure).

Transition probability Probability that controls the move from one state to the next one in a Markovian Monte Carlo process.

Definition of the Subject

Monte Carlo simulation in statistical physics uses powerful computers to obtain information on the collective behavior of systems of many interacting particles, based on the general framework of classical or quantum statistical mechanics. Typically these systems are too complex to allow for a reliable treatment (i.e. with errors that can be controlled) by analytical theory. Monte Carlo simulation uses (pseudo)-random numbers generated also on the computer, and hence is suitable to

derive estimates of probability distributions and averages derived from them. Such probability distributions (such as the so-called "canonical" distribution characterizing the equilibrium state of matter at a given temperature and volume) are the basic objects of statistical thermodynamics. While the latter field of physics provides a convenient formal framework, it does in most cases not yield a convenient tool for explicit calculation, and such an approach is provided by Monte Carlo simulation. In fact, already the first application of the Metropolis importance sampling algorithm in 1953 addressed a problem of this kind, namely the equation of state of hard disks. Since then Monte Carlo simulation has become an extremely useful and versatile tool of statistical physics, with applications varying from many subfields of physics (from condensed matter (i.e. liquids and solids) to elementary particles) to neighboring fields (physical chemistry, theoretical biology, stochastic modeling of complex phenomena in society such as traffic flows, stock market fluctuations, etc.), where methodologies "borrowed" from physics are increasingly applied.

Introduction

One important problem of statistical physics is the explanation of the macroscopic properties of solids, liquids and gases in terms of the atomistic description: 1 cm^3 of a solid contains about $N=10^{22}$ atoms, which in turn are composed of electrons and nuclei. The basic interactions keeping the atoms together are the Coulomb forces between particles of opposite electrical charge, and these Coulomb forces are also responsible for effective forces acting between atoms as a whole. In the present article, we are not concerned with the quantum-mechanical problem of predicting these forces, but rather assume them to be known, and deal only with the many-body problem of interacting atoms in the framework of classical statistical mechanics. Macroscopic properties (e.g., the density ρ of a fluid, the magnetization density m of a ferromagnet, etc.) will be denoted as "observables" $A(X)$ which depend on the degrees of freedom of the N particles (these

degrees of freedom are formally denoted as a vector $\mathbf{x}$, which encompasses the configurational “phase space” of the system). Statistical thermodynamics then shows that in a thermal equilibrium state that is characterized by parameters such as temperature T , pressure p etc., averages $\langle A \rangle$ are to be computed as

$$\langle A \rangle = \int d\mathbf{X} P_{\text{eq}}(\mathbf{X}) A(\mathbf{X}), \quad (1)$$

where $P_{\text{eq}}(\mathbf{X})$ the probability that in equilibrium the “microstate” (=point in phase space) $\mathbf{X}$ occurs. E.g., when the equilibrium of a system is characterized by given volume V and given T , then $P_{\text{eq}}(\mathbf{X})$ is described by the so-called “canonic distribution”

$$P_{\text{eq}}(\mathbf{X}) = (1/Z_N) \exp[-H(\mathbf{X})/k_B T], \quad (2)$$

where $Z_N = \int d\mathbf{X} \exp[-H(\mathbf{X})/k_B T]$ is called “partition function,” k_B is Boltzmann’s constant, and the “Hamiltonian” $H(\mathbf{X})$ describes the interaction energies among the particles (and possible contributions to the energy due to external fields). For N particles in d -dimensional space Eq. (1) would involve a dN -dimensional integral, and in general the task posed by Eqs. (1) and (2) cannot be carried out analytically. Only when the particles do not interact (i.e., an ideal gas, or related problems such as a harmonic solid where one can reduce the problem to an ideal gas of “phonons” describing the lattice vibrations, etc.), is the problem easily tractable, since the multidimensional integration factorizes. In the case of interactions, analytically soluble problems are extremely rare. E.g., the famous Ising model of ferromagnetism

$$H = - \sum_{i \neq j} J_{ij} S_i S_j - H \sum_i S_i, \quad S_i = \pm 1, \quad (3)$$

where the first term on the right hand side describes the exchange interaction between spins at lattice sites i, j of a crystal lattice, while the second term describes the energy due to an external magnetic field, can be solved (in the case of the interaction J_{ij} being nonzero only for nearest neighbor pairs on the lattice) in $d = 1$, but there

the system stays paramagnetic at all temperatures. In $d = 2$ dimensions and $H = 0$, one also can solve the problem, though this requires very tedious and subtle mathematics, but no solution is known in either $d = 2$ or $d = 3$ for any more complicated cases ($H \neq 0$, J_{ij} nonzero for next nearest or even more distant neighbors; etc.). An approximate solution, where the pairwise interaction is reduced to a coupling to an effective mean field (one puts $S_i S_j \approx S_i \langle S_j \rangle + \langle S_i \rangle S_j - \langle S_i \rangle \langle S_j \rangle$) would reduce the problem to an effective single-particle problem, similar to the problem of the ideal paramagnet (for which $Z_N = Z_1^N$). However, comparison with the exactly known cases in $d = 1$ and $d = 2$ shows that this mean field approximation is unsatisfactory, the obtained results may be even qualitatively wrong (such as the prediction of ferromagnetism for $d = 1$), and uncontrollable errors occur. In almost all cases of the statistical mechanics of many interacting degrees of freedom, no analytical tools exist to solve the problem either exactly or approximately with errors that can always be controlled (in particular near the phase transitions).

Monte Carlo simulation amounts to replacing the integration in Eq. (1) by a summation over a representative statistical sample of M points $\{\mathbf{X}_v\}$ that is suitably chosen (what this actually means, will be discussed in the next section). The choice of this sample requires random numbers, which are produced on the computer via a pseudorandom number generator (RNG). These random numbers must be uniformly distributed between zero and unity, and should be uncorrelated. Actually, all random numbers due to RNG’s exhibit some residual correlations, which may cause erroneous results in Monte Carlo simulations, and hence devising “good” RNG’s is a matter of longstanding concern (e.g., (James 1990; Knuth 1969; Mascagni and Srinivasan 2000)). Of course, due to the finiteness of M there occurs the so-called “statistical errors” (as a matter of fact, for some algorithms statistical and systematic errors are not easy to disentangle, see Landau and Binder 2005); but by making M bigger and bigger, these errors can be made smaller and smaller, and hence controlled, and techniques exist to estimate these errors reliably (Berg 2004).

Of course, the application outlined above refers only to a subset of problems in statistical physics, but many other problems can be reduced to it. E.g., the problem of computing averages in quantum statistical mechanics can be reduced to Eqs. (1 and 2) by path-integral Monte Carlo (PIMC) methods (Ceperley 1996; Landau and Binder 2005; Suzuki 1982). In this method, the quantum character of particles enters, on the one hand, by replacing each quantum particle by a chain of classical particles (the coordinate along the chain is the “imaginary time” coordinate of the path integral formalism).

While in this way the delocalization of quantum particles at low temperatures (note that Heisenberg’s uncertainty principle forbids to specify both the spatial coordinates and the momentum of a quantum particle precisely) is elegantly taken into account, the statistics of the particles (for fermions the wave functions need to be strictly antisymmetric with respect to the interchange of coordinates for any pair of particles) is still a challenge for such quantum Monte Carlo methods (Ceperley 1996).

Also seemingly unrelated problems, such as the theory of elementary particles which is a field theory of matter fields on the femtometer scale and of gauge fields respecting the basic symmetry principles of relativistic quantum field theory, can be cast into a form closely related to Eqs. (1) and (2). The generating functional

$$Z = \int \mathcal{D}A \mathcal{D}\bar{\psi} \mathcal{D}\psi \exp[-S_g(A, \bar{\psi}, \psi)] \quad (4)$$

formally corresponds to the partition function in statistical mechanics. Equation (4) involves functional integration over the gauge fields (here A stands symbolically for the vector potential of electrodynamics in the four-dimensional continuum, 3 space + 1 time dimensions) and over the fermionic matter field (described symbolically by ψ and $\bar{\psi}$). The action S_g of the theory contains a coupling constant g which is related to inverse temperature, when one invokes the analogy to statistical mechanics. In fact, to remove ultraviolet divergences that would otherwise plague this quantum field theory one replaces the

fourdimensional continuum by a lattice and hence the theory is called “lattice gauge theory” (Montvay and Münster 1994). Monte Carlo simulations based on this formalism promise to become a powerful approach to unravel the properties of hadrons and other elementary particles, beyond the regime of parameters where analytical theories based on systematic expansions in terms of small parameters (“perturbation theory”) work.

While both in the case of Eqs. (2) and (4) the explicit probability distribution of the interacting many-particle system needs to be constructed itself in the course of the Monte Carlo sampling, via Importance Sampling methods (as will be described in the next section), there exist also simpler cases where a generation of “microstates” of the N -particle system is straightforward, but the analysis of the properties of these microstates is difficult and hence requires large scale simulation. As an example, we mention the “percolation problem” (Stauffer and Aharony 1994). Suppose a ferromagnet, described by Eq. (3), is randomly diluted with non-magnetic atoms, such that a lattice site i carries a spin S_i with probability p and no spin with probability $1 - p$, J_{ij} being non-zero only between nearest neighbor pairs of spins. Then a ferromagnetic ground state of the lattice is only possible if p exceeds the “percolation threshold” p_c , where for the first time an infinite “percolating cluster” of magnetic atoms connected by “bonds” J_{ij} and extending throughout the whole lattice occurs. Choosing random numbers η uniformly distributed between zero and unity, a chosen site is taken by a magnetic atom if $\eta < p$ and otherwise it is taken by a nonmagnetic atom. All lattice sites are occupied independently of each other and all configurations of the lattice generated in this way have equal a priori probability. While the generation of a sample of states by such a “simple random sampling” strategy hence is straightforward, the analysis of the (fractal) percolation clusters near the percolation threshold is a difficult task. Note that many other problems where simple sampling suffices exist (e.g. generation of random walks on lattices, a problem arising in the context of simulating flexible macromolecules, or of diffusion processes). However, we shall not dwell on simple sampling

further but rather refer to the literature (Binder and Heermann 2002; Landau and Binder 2005).

The Metropolis Importance Sampling Algorithm as a Tool in Classical Equilibrium Statistical Mechanics

If we would choose microstates X of a many-body system according to a simple sampling strategy to sample Eq. (2), we would fail to get useful results, except for very small values of N . In fact, the probability distribution $P_{\text{eq}}(X)$ has a very sharp peak in phase space where all extensive variables (extensive variables are proportional to N for $N \rightarrow \infty$) $A(X)$ are close to their average values $\langle A \rangle$. This peak may be approximated by a Gaussian centered at $\langle A \rangle$, with a relative half-width of order $1/\sqrt{N}$. Hence, for a practically useful method, one should not sample the phase space uniformly, but the points X_v over which the sampling is extended must be chosen preferentially from the important region of phase space, i.e., the vicinity of the peak of this probability distribution. This goal is achieved by the importance sampling method (Metropolis et al. 1953): One generates a Markov chain of M configurations X_v , in terms of a Markovian transition probability $W(X_v \rightarrow X'_v)$ that rules the “Monte Carlo moves” from an old state X_v to a new state X'_v . Starting from some (arbitrary) initial state X_1 one creates a “random walk through phase space,” choosing W such that in the limit of $M \rightarrow \infty$ a point X_v , is chosen with a probability proportional to $P_{\text{eq}}(X)$, and hence the average in Eq. (1) is approximated by a simple arithmetic average,

$$\bar{A} = (M - M_0)^{-1} \sum_{v=M_0+1}^M A(X_v) \quad (5)$$

Here it is anticipated that in practice it is better to eliminate the residual influence of the initial state X_1 by eliminating the first $M_0 \gg 1$ states from the average. A condition sufficient to ensure that the points X_v are actually chosen proportional to the desired probability $P_{\text{eq}}(X_v)$ is known as the detailed balance principle,

$$P_{\text{eq}}(X)W(X \rightarrow X') = P_{\text{eq}}(X')W(X' \rightarrow X). \quad (6)$$

Detailed considerations of how the Monte Carlo moves $X \rightarrow X'$ need to be chosen and why the Monte Carlo method actually converges to Eq. (2) can be found in the literature (Binder and Heermann 2002; Frenkel and Smit 2002). Here we only emphasize that one major disadvantage of this method is that knowledge on the normalization factor of $P_{\text{eq}}(X)$, the partition function Z (Eq. (2)), is lost. This is unfortunate, since from Z one could obtain the free energy F via $F = -k_B T \ln Z$, as well as the entropy. Finding ways of obtaining F via alternative sampling algorithms, that yield directly information on the energy density of states, is an active area of research (see “Bibliography” and Landau and Binder (2005)).

It needs also to be pointed out that this Metropolis method can be used for sampling any distribution $P(X)$: one simply has to choose a transition probability $W(X \rightarrow X')$ that satisfies a detailed balance condition with $P(X)$ rather than $P_{\text{eq}}(X)$ as given in Eq. (2).

We continue by giving some comments on the practical implementation of Monte Carlo algorithms. One obvious question is, what is meant in practice by the transition $X \rightarrow X'$. However, there is no general answer to this question: the choice of the move may depend both on the model under consideration and the simulation purpose. Since Eqs. (2) and (6) imply that $W(X \rightarrow X')/W(X' \rightarrow X) = \exp(-\delta H/k_B T)$, δH being the energy change caused by the move from X to X' , typically it is necessary to carry out small changes $\delta X = X' - X$ only. This is achieved in practice by moving only one (or a few) degrees of freedom at a time. Only in rare cases (“cluster algorithms” for Ising models, “pivot algorithm” for self-avoiding walks, etc.) is it possible to find algorithms involving a large δX . It is also useful to realize that often $W(X \rightarrow X')$ can be written as a product of an “attempt frequency” times an “acceptance rate.” By clever choice of the attempt frequency it is sometimes possible to attempt larger moves and still have a high acceptance and thus make the computations more efficient.

The types of Monte Carlo moves can also be adjusted to the choice of statistical ensemble that one wishes to realize. E.g., for a grandcanonical ensemble the chemical potential μ (in addition to volume V and temperature T) is a given variable. Suitable moves then include particle insertions and deletions, i.e., the particle number N in the simulation box fluctuates, as well as the pressure p (which can be sampled e.g. using the virial theorem). Conversely, choosing the NpT ensemble one must include moves where the volume V of the system changes, $V \rightarrow V' = V \pm \Delta V$. Also the chemical potential then fluctuates (and can be sampled using the Widom particle insertion method). For details on all these aspects, we refer to more detailed textbooks (Frenkel and Smit 2002; Landau and Binder 2005).

Another arbitrariness concerns the order in which particles are selected for considering a move. E.g., simulating a lattice model one may go through the lattice in a typewriter fashion. Sometimes it is advisable to use sublattices, e.g. the “checker board algorithm” where white and black sublattices are updated alternatively to allow an efficient “vectorization” of the code. However, if the simulation purpose is to extract dynamic information (invoking the interpretation of the Markov chain in terms of a master equation as will be discussed below), it is better to choose lattice sites (or particle labels, respectively) at random.

We briefly mention the practical realization of the algorithm, choosing the Ising model (Eq. (3)) as a simple example. Then the move $\mathbf{X} \rightarrow \mathbf{X}'$ simply may be a single spin flip $\{S_i \rightarrow -S_i\}$, for instance. The transition probability can be chosen as

$$W(\mathbf{X} \rightarrow \mathbf{X}') = \begin{cases} \exp(-\delta H/k_B T) & \text{if } \delta H > 0 \\ 1 & \text{otherwise.} \end{cases} \quad (7)$$

One compares W for this trial move with a random number η , uniformly distributed in the interval $0 < \eta < 1$; if $W < \eta$, the trial move is rejected and the old state is counted once more in the average. Then another trial is made. If $W > \eta$, on the other hand, the trial move is accepted, and

the new configuration thus generated is taken into account in the average, and serves as a starting point for the next step.

Since successive states $\mathbf{X}_v$ in this process differ only very little, e.g. by a single spin flip in the case of the Ising model, they are highly correlated. Therefore, it is not straightforward to estimate the error of the average. Let us assume that only every n th step is included in the average, and that after n steps these correlations have completely died out. Then the standard estimate for the statistical error $\overline{(\delta A)^2}$ of $\bar{A} = (\tilde{M}^{-1}) \sum A_k$ with $\tilde{M} = (M - M_0)/n$, $A_k = A(\mathbf{X}_v)$ with $v = kn$, applies

$$\overline{(\delta A)^2} = [\tilde{M}(\tilde{M} - 1)]^{-1} \sum_{k=1}^{\tilde{M}} (A_k - \bar{A})^2, \quad \tilde{M} \gg 1. \quad (8)$$

However, the judgment when correlations have died out is subtle (see next section), and great care is needed to derive reliable error estimates (Berg 2004).

The Dynamic Interpretation of Monte Carlo Simulation and Application to Study Dynamic Processes

Often it is useful to associate a time variable t to the index v of successively generated states and to discuss the probability $P(\mathbf{X}, t)$ that a state $\mathbf{X}$ occurs at time t . This probability evolves according to the following master equation

$$\frac{d}{dt}P(\mathbf{X}, t) = - \sum_{\mathbf{X}'} W(\mathbf{X} \rightarrow \mathbf{X}')P(\mathbf{X}, t) + \sum_{\mathbf{X}'} W(\mathbf{X}' \rightarrow \mathbf{X})P(\mathbf{X}', t). \quad (9)$$

Obviously the probability $P(\mathbf{X}, t)$ decreases due to all processes that lead away from the considered state $\mathbf{X}$ (first sum on the right hand side of Eq. (9)), while it increases due to all processes that lead to the considered state from other states $\mathbf{X}'$ (second sum on the right hand side of Eq. (9)). Thus, Monte Carlo sampling (i.e., the sequence of generated

states $X_1 \rightarrow X_2 \rightarrow \dots \rightarrow X_v \rightarrow X_{v+1} \rightarrow \dots$) can be interpreted as a numerical realization of a stochastic time evolution described by the master equation, Eq. (9).

Of course, the units of the “time” in Eq. (9) are not in an obvious way related to the units of physical time (as it appears in the Newtonian equation of motion or in the Schrödinger equation, respectively). Thus, it is common practice to normalize the “Monte Carlo time unit” such that in a system with N particles one attempts N single particle moves per unit time. This is called “one Monte Carlo step (MCS).”

For the thermal equilibrium distribution $P(X, t) = P_{\text{eq}}(X)$, Eq. (2) there is no change of probability with time according to Eq. (9), since the right hand side of Eq. (9) vanishes because of the detailed balance principle, Eq. (6). Thus, thermal equilibrium arises as the stationary solution of the master equation. Markov processes for which Eq. (9) holds involve a relaxation toward thermal equilibrium.

The time evolution of a physical system (whose trajectory through phase space, according to classical statistical mechanics follows from Newton’s equations of motion) in general will differ from the time evolution that follows from Eq. (9), a stochastic rather than deterministic trajectory through phase space. For example, Eq. (9) never describes any propagating modes such as sound waves in a fluid, phonons in a crystal, etc.

Nevertheless, often the trajectory described by Eq. (9) does have physical significance: this is because often one does not wish to describe the full set of dynamical variables of a system, but rather a subset only: for instance, in a solid where diffusion occurs via hopping of atoms over energy barriers to the vacant lattice sites, the mean time between successive hops is orders of magnitude larger than the time scale of atomic vibrations. The latter can be well approximated as a heat bath, as far as diffusion is concerned, and – at least in principle – the transition probability in Eq. (9) describing such a hopping process in a solid can be estimated either by Molecular Dynamics methods or by approximate analytic methods such as transition state theory.

There are many examples where such a separation of time scales for different degrees of freedom occurs. As a rule of thumb, any slow relaxation phenomena may be modeled by Monte Carlo: kinetics of nucleation, spinodal decomposition in alloys, growth of ordered domains in superstructure solids or in adsorbed mono-layers on surfaces, kinetic growth of rough interfaces, etc. Of course, one must pay attention to build in the relevant conservation laws into the model properly (e.g., in a binary metallic alloy the number of atoms of both species A,B is conserved, while the number of vacancies and interstitials may not be conserved). Often (such as in surface diffusion processes) it is not a priori obvious what are the elementary steps that one needs to include into such a “kinetic Monte Carlo” study, and for a realistic description of their rates extensive electronic structure calculations may be needed, in order to be able to connect the Monte Carlo time unit to physical time.

There are also some cases where a Monte Carlo description is a borderline case, as far as the faithful modeling of relaxation phenomena is concerned. E.g., macromolecules in polymer melts undergo Brownian motion (described approximately by analytic models such as Rouse or reptation models, respectively). In such a case, the heat bath for the slow conformational transitions of the polymer is provided by the fast bond-length and bond angle vibrations. However, a Monte Carlo description is not useful for the modeling of polymer melts under flow (Binder 1995). Even if one is not interested in any dynamic properties of the model that is simulated by Monte Carlo, one should be aware of important consequences of Eq. (9). Since Eq. (9) implies that the arithmetic average Eq. (5) has the meaning of a time average ($t_M = M/N$, $t_{M_0} = M_0/N$, $A(X_v) \equiv A(t)$)

$$\bar{A} = (t_M - t_{M_0})^{-1} \int_{t_{M_0}}^{t_M} A(t) dt, \quad (10)$$

“ergodicity” is a problem here, as it is for Molecular Dynamics simulations. By “ergodicity” it is meant that time averages and ensemble averages agree, in the limit of large enough

time intervals $t_M - t_{M_0}$. However, near a first order transition where (in the thermodynamic limit $N \rightarrow \infty$) several phases may coexist, each of these phases plays the role of a separate “ergodic component” from which a trajectory never escapes to another ergodic component. A consequence of this problem is the observation of hysteresis. Sometimes the considered Monte Carlo moves do not even allow one in principle to reach all the states X_v (a well-known example includes algorithms with local moves for self-avoiding walks on lattices, see Binder (1995)). Also problems occur where the system develops a “rugged free energy landscape,” e.g., spin glasses (Binder and Young 1986), where a spectrum of relaxation times develops that spans many decades of time. Similar as in experiments, one then may observe phenomena such as “aging” in a Monte Carlo simulation, and it is difficult to judge whether or not thermal equilibrium has been reached.

Time-displaced correlation functions $\langle A(t)B(0) \rangle$ described by Eq. (9) are then estimated as

$$\overline{A(t)B(0)} = (t_M - t - t_{M_0})^{-1} \int_{t_{M_0}}^{t_M - 1} A(t+t')B(t') \times dt'. \quad (11)$$

Apart from its interest for the study of dynamical properties of the considered models, Eq. (11) is useful to interpret the error due to the correlation between subsequently generated configurations. When we do not assume that subsequent A'_k s in Eq. (8) are uncorrelated, we rather obtain

$$\begin{aligned} \langle (\delta A)^2 \rangle &= \left\langle \left[\frac{1}{\hat{M}} \sum_{k=1}^{\hat{M}} (A_k - \langle A \rangle) \right]^2 \right\rangle \\ &= \frac{1}{\hat{M}} \left\{ \langle A^2 \rangle - \langle A \rangle^2 + 2 \sum_{k=1}^{\hat{M}} \left(1 - \frac{k}{\hat{M}} \right) [\langle A_0 A_k \rangle - \langle A \rangle^2] \right\}. \end{aligned} \quad (12)$$

Now we remember that a time $t = k\delta t = k(n/N)$ is associated with the k th state, and transform the sum in Eq. (12) to a time integral

$$\begin{aligned} \langle (\delta A)^2 \rangle &= \frac{1}{\hat{M}} [\langle A^2 \rangle - \langle A \rangle^2] \\ &\times \left\{ 1 + \frac{2}{\delta t} \int_0^{t_M} \left(1 - t/t_M \right) \phi_{AA}(t) dt \right\}, \end{aligned} \quad (13)$$

where a relaxation function ϕ_{AA} has been introduced,

$$\phi_{AA}(t) = [\langle A(0)A(t) \rangle - \langle A \rangle^2] / [\langle A^2 \rangle - \langle A \rangle^2]. \quad (14)$$

Defining a relaxation time

$$\tau_{AA} = \int_0^\infty \phi_{AA}(t) dt \quad (15)$$

one finds for $\tau_{AA} \ll \tilde{M}\delta t = t_{\text{obs}}$, the “observation time” of the system during the course of the simulation, that

$$\begin{aligned} \langle (\delta A)^2 \rangle &= \frac{1}{\hat{M}} [\langle A^2 \rangle - \langle A \rangle^2] (1 + 2\tau_{AA}/\delta t) \\ &\approx 2(\tau_{AA}/\tau_{\text{obs}}) [\langle A^2 \rangle - \langle A \rangle^2], \end{aligned} \quad (16)$$

where in the last step we have assumed $\tau_{AA} \gg \delta t$. Comparing to Eq. (8), we see that the error is enhanced by a “dynamic factor” $1 + 2\tau_{AA}/\delta t$ (or, equivalently, one has to choose δt so large that $\tilde{M} = \tau_{\text{obs}}/\tau_{AA}$, to avoid correlations between subsequent states). Near critical points of second-order phase transitions, τ_{AA} diverges (“critical slowing down,” see Hohenberg and Halperin (1977) for a detailed discussion).

For a discussion of nonlinear relaxation processes, it is useful to consider the evolution of averages $\langle A(t) \rangle$,

$$\begin{aligned} \langle A(t) \rangle &= \sum_X P(X, t) A(X) \\ &= \sum_X P(X, 0) A(X(t)). \end{aligned} \quad (17)$$

Here we used the interpretation that the ensemble average involved is an average over an ensemble of

initial states (weighted by $P(X, 0)$), which evolve according to Eq. (9). In practice, Eq. (17) means an average over a large number $n_{\text{run}} \gg 1$ of statistically independent runs, $[\bar{A}(t)]_{\text{av}} = n_{\text{run}}^{-1} \sum_{\ell=1}^{n_{\text{run}}} A(t, \ell)$, where $A(t, \ell)$ is the observable A recorded at time t in the ℓ th run. Then nonlinear relaxation functions $\phi_A^{(n\ell)}(t)$ and relaxation times $\tau_A^{(n\ell)}$ are defined as

$$\phi_A^{(n\ell)}(t) = \frac{[\langle A(t) \rangle - \langle A(\infty) \rangle]}{\times / [\langle A(0) \rangle - \langle A(\infty) \rangle]}, \quad (18)$$

$$\tau_A^{(n\ell)} = \int_0^\infty \phi_A^{(n\ell)}(t) dt. \quad (19)$$

Note that the condition that enough states M_0 at the beginning of the Monte Carlo sampling were omitted to eliminate the possible influence of the starting state X_1 , reads $t_{M_0} \gg \tau_A^{(n\ell)}$. Again, however, care is needed when one studies second-order phase transitions: then nonlinear relaxation functions may exhibit power law behavior rather than exponential decay to equilibrium. E.g., for an Ising model in thermal equilibrium we have (Landau and Binder 2005) for the magnetization $m(t)$ and susceptibility $\chi(t)$ [assuming one starts from a perfectly aligned state at T_c , and $N \rightarrow \infty$]

$$m(t) \propto t^{-\beta/z\nu}, \quad \chi(t) \propto t^{\gamma/z\nu}, \quad t \rightarrow \infty, \quad (20)$$

where β , γ are the critical exponents of the order parameter and susceptibility in thermal equilibrium (assuming a d -dimensional lattice of size L for $L \rightarrow \infty$)

$$\begin{aligned} \langle |m| \rangle &\propto (1 - t/T_c)^\beta, \chi \\ &\equiv L^d [\langle m^2 \rangle - \langle |m| \rangle^2] \propto |1 - T/T_c|^{-\gamma}, \end{aligned} \quad (21)$$

while ν and z are the critical exponents of the correlation length ξ and the relaxation time τ_{mm} ,

$$\xi \propto |1 - T/T_c|^{-\nu}, \quad \tau_{mm} \propto \xi^z. \quad (22)$$

Also the nonlinear relaxation time diverges $\{\tau_m^{(n\ell)} \propto \xi^{z-\beta/\nu}\}$. In fact, testing for Eq. (20) is a possible approach to study critical phenomena by

Monte Carlo methods, avoiding the need to equilibrate the system (“nonequilibrium relaxation method”). However, this approach requires the use of very large systems, since all critical divergences considered in Eqs. (21) and (22) are rounded off when the correlation length $\xi(t)$ (which grows as $\xi(t) \propto t^{1/z}$, see Sadiq and Binder 1984) has grown to a value comparable to L . Such finite size effects are also important to consider in the context of equilibrium Monte Carlo studies, as will be discussed in the next section. Note also that power law growth of fluctuations also occurs for $T < T_c$, when we start an Ising model in a disordered spin configuration, domains grow according to a relation $\ell(t) \propto t^{1/2}$ for their linear dimension and (Sadiq and Binder 1984)

$$\chi(t) \propto t^{d/2}. \quad (23)$$

Then equilibrium is reached only when $\ell(t) \approx L$, implying that $\tau_m^{(n\ell)} \propto L^2$. This consideration shows that the choice of the initial state in Monte Carlo sampling also should be done with care: for $T < T_c$ equilibrium is reached much faster if we start from a well-ordered initial state, of course.

Overcoming the Limitations of Finite Size

While systematic analytic expansions or closed-form approximations often are useful for systems away from phase boundaries where first- or second-order phase transitions occur, such methods often are of doubtful value near phase transitions. Thus, the study of phase transitions is one of the most important fields where Monte Carlo simulations are useful and important. However, sharp phase transitions occur in the thermodynamic limit only, $N \rightarrow \infty$. Of course, this is no problem for real systems: even a small water droplet freezing into a snowflake may still contain $N=10^{18}$ water molecules, and thus the relative shift and rounding of the transition are of order $N^{-1/3}=10^{-6}$ and $N^{-1/2}=10^{-9}$, respectively. But the situation is different for simulations, where an economical use of computer resources requires to study rather small systems (of order $N=10^2$ to $N=10^6$ are typical), and hence finite size effects need careful consideration (Binder and Heermann 2002).

It turns out, however, that these finite size effects are not just only a limitation, but also a valuable tool to infer properties of the infinite system from the finite size behavior. As an example, we discuss the phase transition of the Ising ferromagnet (Fig. 1), which has a second-order transition at a critical temperature T_c , with critical behavior as characterized by Eqs. (21) and (22). In a finite system, of course, ξ cannot exceed L , and hence these critical singularities are smeared out. Now finite size scaling theory (Fisher 1971; Privman 1990) implies that such finite size effects can be understood from the principle that “ L scales with ξ .” Hence it is plausible that the magnetization probability $P_L(m)$ can be written (Binder 1981)

$$P_L(m) = L^x \tilde{P}(L/\xi, mL^x), \quad x = \beta/\nu. \quad (24)$$

Here $P_L(m)$ satisfies the normalization $\int dm P_L(m) = 1$, $\tilde{P}$ is a scaling function, and the result $x = \beta/\nu$ follows from the fact that

$$\langle |m| \rangle = L^{-x} \tilde{m}(L/\xi) = L^{-\beta/\nu} \tilde{m}(L/\xi) \quad (25)$$

for $L \rightarrow \infty$ must reduce to $\langle |m| \rangle \propto \xi^{-\beta/\nu}$. This is only possible when $\tilde{m}(\xi \rightarrow \infty) \propto \xi^x$ to cancel the power of L and when $x = \beta/\nu$. Since similarly $\langle |m|^k \rangle = L^{-k\beta} \tilde{m}_k(L/\xi)$, one derives a similar scaling relation for the susceptibility,

$$\begin{aligned} k_B T \chi &\equiv L^d \left(\langle m^2 \rangle - \langle |m| \rangle^2 \right) \\ &= L^{\gamma/\nu} \tilde{\chi}(L/\xi), \end{aligned} \quad (26)$$

where the hyperscaling relation $\gamma/\nu = d - 2\beta/\nu$ was invoked, and $\tilde{\chi}(\xi) \equiv \tilde{m}_2 - \tilde{m}^2$. The fourth order cumulant U_L is a function of L/ξ only,

$$U_L = 1 - \langle m^4 \rangle / [3 \langle m^2 \rangle^2] = \tilde{U}(L/\xi). \quad (27)$$

For $T > T_c$ and large L the distribution $P_L(m)$ tends to a gaussian and hence $U_L \rightarrow 0$; for the double-gaussian distribution for $T < T_c$, however, $U_L \rightarrow 2/3$. For $T = T_c$ finite size scaling implies $U_L = \tilde{U}(0)$, independent of L . As a consequence, when one studies U_L as a function of temperature for different choices of L one should find T_c from a

common intersection point. This “cumulant intersection method” has become a very widespread and useful tool for the study of critical phenomena (Binder and Heermann 2002).

Also the analysis of $P_L(m \approx 0)$ for $T < T_c$ is very useful (Binder 1982). The state of the system then is dominated by a twophase configuration, i.e. (because of periodic boundary conditions) a slab-like domain with negative magnetization is separated from a domain with positive magnetization by two interfaces of area L^{d-1} . As a consequence, the deep minimum of $P_L(m \approx 0)$ in Fig. 1 is described by

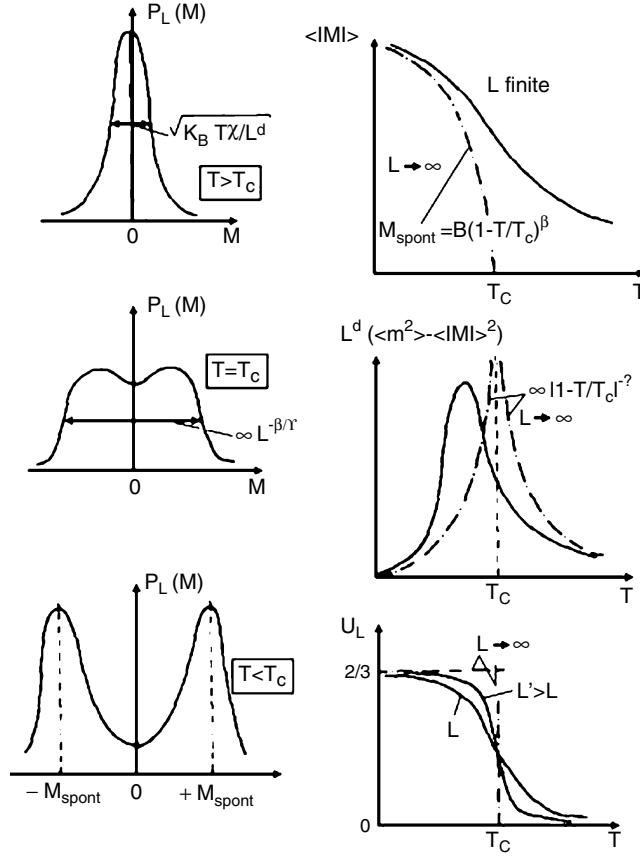
$$\ln[P_L(m \approx 0)/P_L(m \approx M_{\text{spont}})] = -2L^{d-1} f_{\text{int}}/k_B T, \quad (28)$$

where $\pm M_{\text{spont}}$ characterizes the peak positions of $P_L(m)$ for $T < T_c$, and f_{int} is the interfacial free energy (per unit area). As a consequence, one can extract estimates for f_{int} from an analysis of $P_L(m \approx 0)$ as well. This approach has also found widespread applications for various systems (including phase separation in simple fluids and fluid mixtures and polymer solutions and blends, colloid-polymer mixtures, etc.).

A simple discussion of finite size effects at first order transitions is similarly possible. The phases coexisting at the first-order transition are again described by gaussians. In a finite system these phases coexist not only right at the transition, but over a finite parameter region. The relative weights of these states are given in terms of the free energy differences of these phases. From this phenomenological description, energy and order parameter distributions and their moments can be derived. One finds that the maximum of specific heat and susceptibility scale proportional to the volume, i.e. $k_B T \chi_{\text{max}} \propto L^d$ (instead of $L^{\gamma/\nu}$ as at a second-order transition, Eq. (26).

Extensions to Quantum Statistical Mechanics

In quantum mechanics, an observable $A(\mathbf{X})$ now is represented by an quantum mechanical operator $\hat{A}$, and hence Eq. (1) is replaced by



Monte Carlo Simulations in Statistical Physics,

Fig. 1 Schematic evolution of the order parameter probability distribution $P_L(m)$ from $T > T_c$ to $T < T_c$ (from above to below, left part), for an Ising ferromagnet (where M is the magnetization per spin) in a cubic box of volume $V = L^d$. The right part shows the corresponding

temperature dependence of the mean order parameter $\langle |M| \rangle$, the susceptibility $k_B T \chi' = L^d(\langle M^2 \rangle - \langle |M| \rangle^2)$, and the reduced fourth-order cumulant $U_L = 1 - \langle M^4 \rangle / [3 \langle M^2 \rangle^2]$. Dashdotted curves indicate the singular variation that results in the thermodynamic limit, $L \rightarrow \infty$

$$\begin{aligned} \langle \hat{A} \rangle &= Z^{-1} \text{Tr} \exp(-\hat{H}/k_B T) \hat{A} \\ &= Z^{-1} \sum_n \langle n | \exp(-\hat{H}/k_B T) | n \rangle, \end{aligned} \quad (29)$$

where $\hat{H}$ is the Hamiltonian of the system, and the states $|n\rangle$ form a complete, orthonormal set. In general, the eigenvalues E_α and eigenstates $|\alpha\rangle$ of the Hamiltonian are not known ($\hat{H}|\alpha\rangle = E_\alpha|\alpha\rangle$), and we wish to evaluate the trace in Eq. (29) without attempting to diagonalize the Hamiltonian. This can be achieved by path-integral Monte Carlo (PIMC); other versions of quantum Monte Carlo methods which focus on finding the ground state and its energy are outside of consideration here.

The basic idea of PIMC can already be explained for the simple case of a single particle in one dimension in a potential $V(x)$. In position representation, the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) = \hat{E}_{\text{kin}} + \hat{V}, \quad (30)$$

where $\hbar$ is Planck's constant. The problem is the fact that the operators of kinetic energy $\hat{E}_{\text{kin}}$ and potential energy $\hat{V}$ do not commute, $[\hat{E}_{\text{kin}}, \hat{V}] \neq 0$. If $\hat{E}_{\text{kin}}$ and $\hat{V}$ commuted, we could replace $\exp[-(\hat{E}_{\text{kin}} + \hat{V})/k_B T]$ by $\exp(-\hat{E}_{\text{kin}}/k_B T) \exp(-\hat{V}/k_B T)$, and by inserting the identity $\hat{1} = \int dx' |x'\rangle \langle x'|$ we would have solved the problem, since

$\langle x | \exp(-\hat{E}_{\text{kin}}/k_B T) | x' \rangle$ amounts to dealing with the (known) quantum mechanical propagator of a free particle. However, by neglecting the non-commutativity of $\hat{E}_{\text{kin}}$ and $\hat{V}$ we would have reduced the problem back to the realm of classical mechanics, all quantum effects would have been lost.

But, a related recipe is provided by the exact Trotter product formula for two non-commuting operators $\hat{A}$ and $\hat{B}$, P being an integer,

$$\exp(\hat{A} + \hat{B}) \rightarrow [\exp(\hat{A}/P)\exp(\hat{B}/P)]^P \quad \text{for } (31)$$

$$P \rightarrow \infty.$$

Using Eq. (31) the partition function can be written as

$$Z = \lim_{P \rightarrow \infty} \int dx_1 \int dx_2 \cdots \int dx_P \langle x_1 | \exp(-\hat{E}_{\text{kin}}/k_B TP) \exp(-\hat{V}/k_B TP) | x_2 \rangle \times \langle x_2 | \cdots \langle x_P | \exp(-\hat{E}_{\text{kin}}/k_B TP) \exp(-\hat{V}/k_B TP) | x_1 \rangle \rangle. \quad (32)$$

Note the matrix elements can be worked out, with the result ($P \rightarrow \infty$)

$$Z = \left(\frac{mk_B TP}{2\pi\hbar^2} \right)^{P/2} \int dx_1 \cdots dx_P \exp \left\{ -\frac{1}{k_B T} \left[\frac{\kappa}{2} \sum_{s=1}^P (x_s - x_{s-1})^2 + \frac{1}{P} \sum_{s=1}^P V(x_s) \right] \right\}, \quad (33)$$

with the boundary condition $x_{P+1} = x_1$ and the effective spring constant $\kappa = mP(k_B T)^2/\hbar^2$. Equation (33) formally corresponds to a classical partition function of a “ring polymer). will P “monomers” Its gyration radius (which is of order $\hbar/\sqrt{mk_B T}$, i.e. of the same order as the thermal de Broglie wavelength $\lambda_T = \hbar/\sqrt{2\pi mk_B T}$ of the quantum particle) represents the region over which the quantum particle typically is delocalized at temperature T . If effects of quantum statistics are ignored (which is admissible for crystals at low T , apart from solid helium) the generalization of this formalism (Eqs. (32) and (33)) to N particles is straightforward. In fact, useful applications to describe low temperature properties of crystals beyond the harmonic

approximation have been given (Landau and Binder 2005). Related approaches also based on the Trotter formula can be developed for various lattice problems, e.g. the Ising model on a d -dimensional lattice in a transverse field can be reduced to an ordinary Ising problem (with no transverse field) on a $(d+1)$ -dimensional lattice, but with anisotropic interactions (the extra lattice direction corresponds to the “imaginary time” coordinate s in Eq. (33) along the contour of the ring polymer). But many problems of physical interest, e.g. the Hubbard Hamiltonian describing strongly correlated fermions on a lattice, cannot yet be satisfactorily simulated by such Monte Carlo methods at low enough temperatures because of the “minus sign problem”: the distribution to be sampled $\{\rho(\mathbf{x})\}$ is not always positive, and hence cannot be interpreted as a probability density suitable for importance sampling. The brute force recipe consists of splitting $\rho(\mathbf{x})$ into its sign (S) and its absolute value ($\tilde{\rho} = |\rho(\mathbf{x})|$), so that $\rho = S\tilde{\rho}$, and then the quantum average can be formally rewritten as

$$\langle A \rangle = \langle AS \rangle_{\tilde{\rho}} / \langle S \rangle_{\tilde{\rho}}, \quad (34)$$

where $\langle \cdots \rangle_{\tilde{\rho}}$ means averaging with $\tilde{\rho}$ as weight function. However, this brute force approach works only for rather small N , since the average of the sign behaves as $\langle S \rangle_{\tilde{\rho}} \propto \exp(-\text{const.} \times N)$. Alleviating this problem is still an active area of research.

Future Directions

There is still very active research going on to find more efficient algorithms, by a clever design of Monte Carlo moves adapted to specific problems, by exploiting advanced computer architecture (e.g. “parallel tempering” methods exploit parallel architectures by running n real replicas of the system at closely spaced neighboring temperatures or other control parameters in parallel and exchanging from time neighboring temperatures, to allow for a faster relaxation of the system configurations), and by techniques such as “multicanonical Monte

Carlo” (Berg 2004) or Wang-Landau sampling of the energy density of states (Landau and Binder 2005) or related methods of so-called “umbrella sampling.” The easy availability of powerful desk-top computers has also facilitated the study of rather complex model systems (unlike the early days of Monte Carlo, where the research had to focus on “toy problems” such as the Ising model, the hard disk and hard sphere fluids, the self-avoiding walk problem, percolation, etc.). While these classic problems still are useful as a testbed for new methodologies of simulation the analysis of simulation output, there is now much emphasis on applications directed towards materials sciences, soft and biological matter, and statistical mechanics far from equilibrium. In this context, also “multiscale simulation” methodology has become a very active field of research: e.g., electronic structure calculation on the subatomic scale is required to yield realistic input for potentials that can then be used for instance in kinetic Monte Carlo simulations. Monte Carlo methods developed in the context of statistical physics are very popular for applications clearly going beyond physics, such as simulations of sociological and economical processes (“econophysics”), biologically motivated models, etc. There also is a continuous and fruitful exchange of know how with the practitioners of other simulation techniques (classical and “ab initio” Molecular Dynamics, Lattice Boltzmann simulations of transport phenomena), unlike in the past where the different “communities” of simulators worked in a rather disjunct manner.

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Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence

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Article Outline

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Glossary

Bifurcation A change from one kind of behavior to another, e.g., a bifurcation from steady flow to time-periodic flow

Defect A location where a pattern abruptly changes, e.g., where a line ends or two lines meet at a point

Deterministic chaos Erratic behavior arising from a low-dimensional, deterministic system; behavior that shows sensitive dependence on initial conditions where a small error in initial conditions grows roughly exponentially in time

Finite-time Lyapunov exponent (FTLE) field A field showing how much fluid parcels are stretched over a small interval of time

Free energy functional An effective energy that depends on the function describing a pattern

Fully developed turbulence Turbulent flow for very large Reynolds number with no spatial or temporal order

Grain boundary Line or curve in a pattern where two different zones meet.

Kolmogorov-Arnold-Moser (KAM) invariant surface Curve or surface that separates region of ordered trajectories from region of chaotic trajectories. Tracers cannot cross between these two regions; consequently, a KAM invariant surface acts as a transport barrier.

Lagrangian coherent structure (LCS) A region in a flow where passive impurities move mostly together, rather than being stretched and mixed with the rest of the flow

Laminar flow Smooth, well-ordered flow, achieved with small Reynolds number

Lévy flights Trajectories characterized by jumps between distant parts of the system. If it is a Lévy flight, the jumps in a trajectory have a probability distribution $P(L) \sim L^{-\mu}$, with $2 < \mu < 3$.

Linear stability theory Approach used to determine critical parameters (e.g., Re or Ra) at which a flow becomes unstable. Linear stability theory also determines the wavenumbers of the disturbances that are unstable.

Lobe (or “turnstile”) Region bounded by the intersection of stable and unstable manifolds. Lobes provide the mechanism for transport of impurities between different regions in a flow.

Manifold (or “invariant manifold”) A collection of points in a flow which, when evolved forward in time, map on to the same collection of points. Manifolds also act as barriers for transport and front propagation.

Poincaré section A stroboscopic plot for a time-periodic or flow showing the positions of one or more tracers once each period of the flow

Rayleigh-Bénard convection A flow that develops from an instability due to unstable stratification when a fluid is heated from below

Rayleigh number Dimensionless parameter that characterizes the magnitude of the temperature difference in a Rayleigh-Bénard flow. The Rayleigh number can also be thought of as a ratio of thermal buoyancy to diffusive damping.

Reaction-diffusion system A spatially extended system that produces patterns or fronts as a result of the interaction between some sort of reaction (e.g., chemical reaction, biological interaction, phase transition) and molecular diffusion.

Reynolds number Dimensionless parameter that characterizes the strength of a flow. The Reynolds number can also be thought of as the ratio between fluid inertia and viscous damping.

Stratification Density variations in a fluid system

Strong turbulence High Reynolds number turbulence

Subdiffusion Transport where the variance σ^2 grows more slowly than normal diffusion, e.g., $\sigma^2(t) \sim t^\gamma$, with $\gamma < 1$. Associated with regions in the flow where the tracers temporarily stick.

Superdiffusion Transport where the variance σ^2 grows more rapidly than normal diffusion, e.g., $\sigma^2(t) \sim t^\gamma$, with $\gamma > 1$. Associated with Lévy flight trajectories.

Taylor-Couette flow Flow between two coaxial cylinders, the inner of which (at least) is rotating

Weak (defect-mediated) turbulence Flows with intermediate values of the Reynolds number that still produce short-range patterns but evolve both spatially and temporally in a complicated manner and can be characterized by the presence of numerous defects in the pattern (more defects for more turbulent flows) that move around the system.

Definition

“Nonlinear dynamics” is the study of systems described by equations of motion that depend nonlinearly on their variables. This is of significant scientific and mathematical interest because nonlinear systems – unlike simpler linear ones – typically show quite complicated behavior, including deterministic chaos, spontaneous formation of patterns, spatiotemporal complexity,

and turbulence. The equations describing fluid flows are nonlinear; consequently, there is a wide variety of types of flows that can be achieved, spanning a wide range of levels of complexity from simple, well-ordered, *laminar* flows up through turbulent flows with significant complexity both in space and time. The equations that describe the mixing of impurities in a flow are also often nonlinear (depending on the fluid flow); consequently, mixing can also be very complicated and even *chaotic*.

Introduction and Theoretical Background

The dynamics of a fluid flow are governed by the Navier-Stokes equation:

$$\frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \vec{u} + \frac{1}{\rho} \vec{F}.$$

This is the fluid continuum version of Newton’s second law. The first term on the left represents the change in a momentum of a small parcel of a fluid. Several factors can result in a change in momentum: forces acting on the fluid element – pressure differences, viscosity, and external forces (first, second, and third terms on the right) – and advection of higher or lower velocity fluid elements into the region of interest (the second term on the left). The Navier-Stokes equation can be nondimensionalized by scaling the velocity by a characteristic velocity scale U , lengths by a typical length scale L , and time by an advective timescale L/U :

$$\frac{\partial \vec{u}'}{\partial t} + \vec{u}' \cdot \nabla' \vec{u}' = -\nabla'(\Delta p)' + \frac{1}{Re} \nabla'^2 \vec{u}'$$

where we have neglected external forcing and where $\vec{u}' \equiv \vec{u}/U$ is the nondimensional velocity. The nondimensional parameter, $Re = UL/\nu$, is the Reynolds number. The Reynolds number characterizes the ratio of inertia to viscosity in a fluid flow.

The advection term on the left is often referred to as the *inertial* term and is the source of nonlinearity in the Navier-Stokes equation. Nonlinearity goes hand-in-hand with complexity;

consequently, the Reynolds number is the fundamental parameter used to describe the transition in fluid flows from simple, laminar (smooth), well-ordered flows to more and more complicated flows. If $Re \ll 1$, the inertial term is negligible and for steady flows, viscosity at every location is balanced by pressure gradients. In this limit, the Navier-Stokes equations can be rewritten (in dimensional form) as:

$$\frac{1}{\rho} \vec{\nabla} p = \nu \nabla^2 \vec{u}$$

Flows in this limit are called *viscous*, *creeping*, or *Stokes* flows. If $Re \gg 1$, viscosity is negligible, and the NS Equation can be written as:

$$\frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \vec{\nabla} \vec{u} = -\frac{1}{\rho} \vec{\nabla} p$$

Flows in this limit are called *inviscid* or *Euler* flows and are dominated by inertial effects. Flows with very large Re are typically turbulent.

There has been significant research into the transition between well-ordered, laminar, viscous flows for $Re \ll 1$ and fully developed turbulent flows for $Re \gg 1$. Landau (1944) predicted that an increase in Re would be accompanied by an infinite series of bifurcations as more and more frequencies of fluid oscillation (and corresponding spatial complexity) are added to the flow. According to Landau, measurement of the flow velocity at a point will reveal a steady, time-independent signal for weak flows (low Re), then for stronger flows, the velocity will oscillate periodically at that point, then at higher Re , the velocity time series at that point will be a superposition of two periodic oscillations with different frequencies. As Re increases, the velocity time series will be a superposition of more and more sinusoidal functions with different frequencies. Ultimately, according to Landau, a turbulent flow is simply one with so many superposed frequencies that it *seems* complicated and unpredictable.

Landau's prediction was tested in the early 1970s by Harry Swinney and Jerry Gollub in a *Taylor-Couette* flow (Gollub and Swinney 1975) (see section "[Taylor-Couette Flow](#)" for more detail about Taylor-Couette flow). However, they

did not find an infinite sequence of transitions with more and more frequencies (and more and more complexity). Instead, they found a sudden transition from an ordered flow with two superposed frequencies directly to broad spectrum, aperiodic time dependence, a state that we now know to be *chaotic*. This direct transition in fluid flows to chaotic time dependence was also predicted theoretically by Ruelle and Takens in 1971 (1971).

Deterministic chaos is denoted by two main features: (1) complicated, aperiodic time dependence from a simple, deterministic system with a small number of degrees of freedom; and (2) sensitive dependence on initial conditions, whereby small uncertainties in measurements of the initial conditions grow roughly exponentially in time, destroying long-term predictability. Despite the name, however, chaotic systems are usually quite well-ordered spatially; it is the time dependence that is complicated. Further increases in Re are needed to break up the spatial patterns that persist for chaotic flows. A regime displaying disorder in both space and time is referred to as *spatiotemporal chaos* or *weak turbulence*. Weak turbulent regimes are still characterized by well-defined structures (e.g., vortices), but the structures are arranged in a disordered pattern. These structures break up if Re is increased beyond that for the weak turbulent regime; ultimately, for large enough Re , the flow is described as *fully developed turbulence* with a broad spectrum of spatial length scales. Long-lived vortex structures may survive for surprisingly large Re , however, especially in planetary and atmospheric flows in rotating systems (Marcus 1988) or in plasma flows with large uniform magnetic fields.

In this entry, we present several different examples of pattern formation, mixing, and chaos in fluid systems. Section "[Specific Examples of Patterns in Fluid Flows](#)" presents specific examples of the kinds of transitions discussed above in fluid flows, showing the patterns that accompany these transitions. We emphasize Taylor-Couette and convective flows, mainly due to their historical importance in this field. In section "[Transport and Mixing](#)," we discuss transport and mixing, highlighting in particular the fact that fluid mixing in *laminar*, well-ordered flows is often

chaotic. Section “[Manifolds, Lobes and Transport Barriers](#)” presents a discussion of manifold and *Lagrangian coherent structure* theories that help elucidate barriers that impede the mixing of passive impurities. In section “[Pattern Formation in Reaction-Diffusion and Advection-Reaction-Diffusion Systems](#),” we discuss chemical pattern formation and front propagation in both stagnant and flowing systems. Section “[Burning Invariant Manifolds and Reaction Fronts](#)” presents an extension of the manifold theory to advection-reaction-diffusion systems, highlighting the one-way barriers that impede the motion of reaction fronts. Section “[Other Examples of Pattern-Forming Systems](#)” contains a brief listing of some other types of pattern-forming systems. We finish in section “[Future Directions](#)” with a brief overview of future directions in the field.

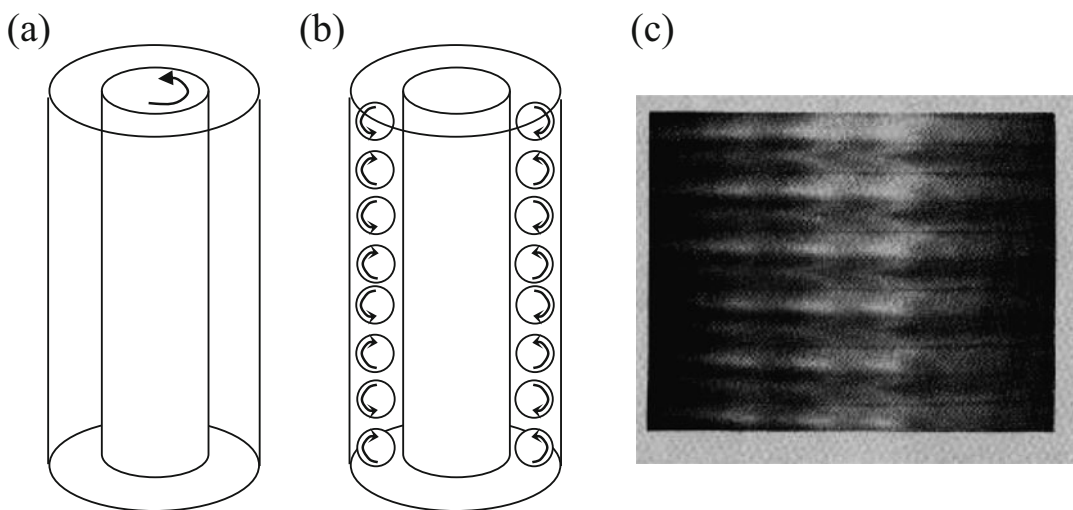
Specific Examples of Patterns in Fluid Flows

There are a number of different flows whose spatial patterns have been studied. Similar patterns are found in a very wide range of flows.

Taylor-Couette Flow

Taylor-Couette flow is the flow between two coaxial cylinders (Fig. 1a). In its simplest form, the outer cylinder remains stationary while the inner cylinder rotates. No-slip boundary conditions require fluid at the outer edge to remain stationary while fluid at the inner edge rotates with the inner cylinder. The Reynolds number for this flow is defined using the gap width L as the length scale and the maximum flow velocity U as the velocity scale: $Re = UL/\nu$. Taylor-Couette flows are often visualized with kalliroscope ([Kalliroscope Corporation](#)), a suspension of aluminum flakes that align with shear zones in the flow. Reflection of light off the flakes depends on their orientation; consequently, kalliroscope quite effectively visualizes the flow field. This technique was originally developed by the artist Paul Matisse but has been adopted by experimentalists who study fluid instabilities.

For small Re in the Taylor-Couette system, flow between the cylinders is laminar and purely in the azimuthal direction, with the velocity magnitude dropping smoothly from the inner cylinder velocity to zero at the outer cylinder. Beyond a critical Re , this smooth flow becomes unstable



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 1 Taylor-Couette flow. (a) Diagram of configuration. The fluid is contained in the gap between two coaxial cylinders, the inner of which (at least) rotates, driving a flow between the two cylinders. (b)

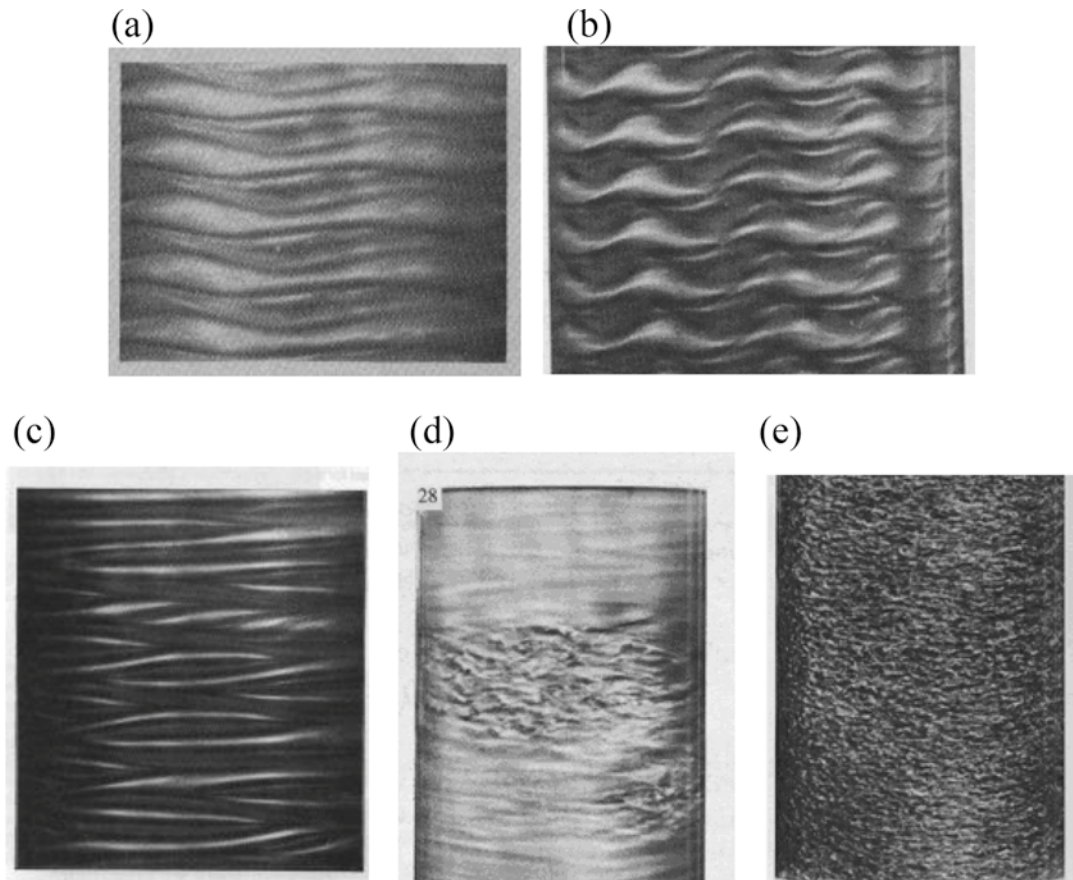
Cross-sectional sketch of Taylor-Couette vortices. (c) Experimental image showing Taylor-Couette vortices; flow is visualized using kalliroscope. (From Fenstermacher et al. 1979)

due to centrifugal effects – the faster moving fluid near the inner cylinder moves outward while the slower moving fluid near the outside moves inward. The result is a pattern of stacked tori (donut-shaped structures) called *Taylor vortices* (Fenstermacher et al. 1979) (Fig. 1b and c). A fluid element within a Taylor vortex still moves azimuthally around the cylinders but also follows a closed (vortex) path in r - z coordinates. A radial cross section of the flow reveals a chain of counter-rotating vortices.

Further increases in Re result in a bifurcation to *wavy vortex* flow (Andereck et al. 1986), where the tori defining the Taylor vortices develop a snake-like undulation that propagates around the

annulus (Fig. 2a). This spatial pattern corresponds to the time-periodic state discussed in transition to chaos in section “[Introduction and Theoretical Background](#).” Further increases in Re result in transitions to quasi-periodic and chaotic states. Ultimately, for large enough Re , the flow is turbulent (Fig. 2e).

If the outer cylinder rotates as well, a wide variety of spatial patterns are found (Andereck et al. 1986, 1983). Some of these states are shown in Fig. 2. Taylor-Couette flows have been studied extensively because of the wide variety of different states, including states in which the flow experiences intermittent (momentary) bursts of turbulence. Various investigators have mapped



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 2 Some examples of Taylor-Couette patterns; all visualized with kalliroscope flakes. (a) Wavy vortex flow (From Fenstermacher et al. 1979); (b) Modulated wavy vortex flow (From Andereck et al.

1986); (c) Braided vortex flow (from Andereck et al. 1983); (d) Intermittent turbulent spots (From Andereck et al. 1986); and (e) Turbulent flow. (From Andereck et al. 1986)

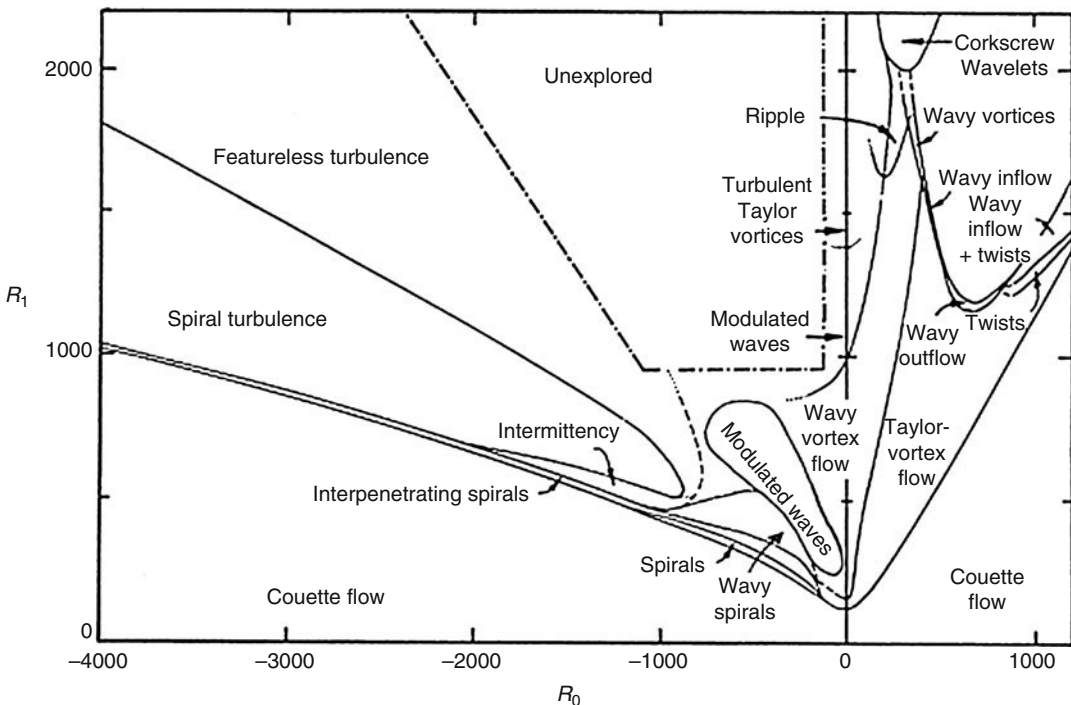
out *parameter space diagrams* that show the conditions needed to obtain various different states in Taylor-Couette flow. An example of such a parameter space diagram (Andereck et al. 1986) is shown in Fig. 3.

Rayleigh-Bénard Convection

When a fluid is heated from below or from the side, the warmer fluid near the bottom expands and becomes less dense than the cooler fluid above. This results in unstable stratification with heavier, more dense fluid above lighter, less dense fluid. If the stratification is large enough, the denser fluid falls and the lighter fluid rises, producing a *convective* flow. Thermal convection of this nature is quite common: it occurs when heating up water or soup on a stove; it is a dominant mechanism by which a heating element heats up the air in an oven or by which heat from a radiator warms up a room; it is the dominant mechanism by which atmospheric flows are driven; it is the mechanism by which flows within

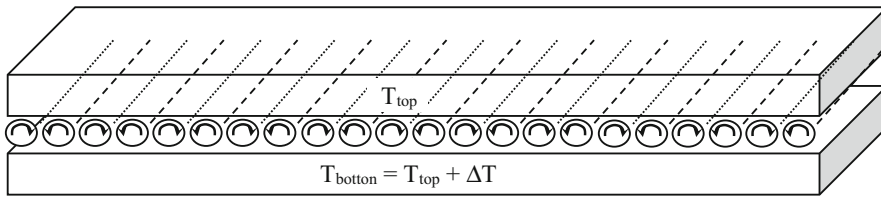
the Earth's crust are formed; and it is a major driving force for flows in stars. In all cases, thermal convection results in *significantly* faster and more efficient transport of heat than would be achieved solely with thermal diffusion.

In its simplest form, thermal convection ensues if a large enough vertical temperature gradient is applied with the bottom warmer than the top (Fig. 4). The relevant dimensionless number characterizing the magnitude of the temperature difference is the *Rayleigh Number*. $Ra = g\alpha\Delta T/\nu\kappa$, where $\Delta T = T_{\text{bottom}} - T_{\text{top}}$ is the temperature gradient, α is the coefficient describing the volume expansion of the fluid in response to a change in temperature, g is the gravitational acceleration, and κ is the thermal diffusivity. Conceptually, increases in the temperature difference, gravitational acceleration, or expansion coefficient make the fluid more unstable, whereas viscosity inhibits fluid motion, and thermal diffusivity tends to diminish temperature differences.



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 3 Parameter space diagram showing the many different regimes of pattern formation for

Taylor-Couette flow between two coaxial cylinders. (From Andereck et al. 1986)



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 4 Schematic for Rayleigh-Bénard convection. A thin layer of fluid is sandwiched between two thermally-conducting plates, with the bottom plate hotter than the top plate. For sufficiently large ΔT , convection ensues with hotter, light fluid rising from the

bottom and colder, denser fluid falling from the top. In its simplest form, the convection pattern is a pattern of counter-rotating “rolls” as shown in the sketch. The dotted (dashed) lines denote “downwelling” (upwelling) regions in the flow

If Ra is small, the fluid remains motionless – viscosity and thermal diffusion are sufficient to keep the fluid from becoming unstable. If Ra exceed a critical value Ra_c , the motionless state becomes unstable and the warmer, less dense fluid near the bottom rises while the cooler, more dense fluid near the top sinks. In a thin, rectangular box, a pattern of *convection rolls* develops, with fluid circulating like rotating cigars in a box, as shown schematically in Fig. 4.

Numerous studies have been made of patterns made by Rayleigh-Bénard convection. In a manner similar to that in Taylor-Couette flow, there is a series of bifurcations from well-ordered to chaotic and ultimately to turbulent flow in Rayleigh-Bénard convection. The nature of the transitions depends not only on the Rayleigh number Ra but also on a second dimensionless parameter called the *Prandtl number* $Pr = \nu/\kappa$ which denotes the relative magnitudes of the viscous and thermal diffusivities and is a property of the fluid used in the experiments. Large Prandtl numbers are achieved in fluids with large viscosities; even water at room temperature has a Prandtl number of around 6. Pressurized gases have Prandtl numbers of around 1. Small Prandtl numbers are achieved in flows of liquid metals (e.g., mercury or sodium) that are very good thermal conductors and flows in gases which have a very small kinematic viscosity.

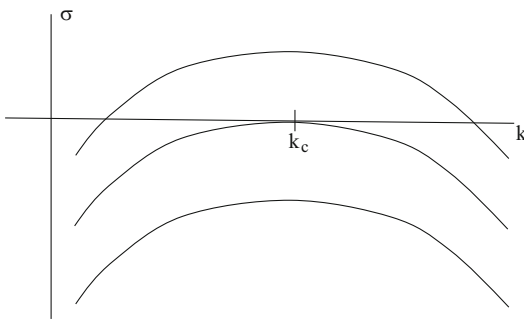
For fluids with small Pr , the first instability from steady (time-independent) convection rolls is an oscillatory instability, similar in many respects to the wavy vortex state for Taylor-Couette flow. The convection rolls form a snake-

like instability along their axes, and this undulation in the rolls propagates in a direction parallel to the axes of the convection rolls. A cross section of the flow in this state would reveal a pattern of counter-rotating vortices that oscillates periodically in the lateral direction.

There are also several other instabilities that appear in Rayleigh-Bénard convection including: cross-roll instabilities in which a second pattern of convection rolls develops perpendicular to the first; a skew-varicose instability in which the width of convection rolls is modulated; a zig-zag instability which is exactly what its name implies, one in which the convection rolls form a zig-zag pattern; an instability referred to as the “Eckhaus instability” where pairs of convection rolls disappear, allowing other rolls present to grow and increasing the wavelength of the pattern; and spiral convection patterns. Defects can also appear in convection patterns where either two or more convection rolls meet at a point. The motion of a defect parallel to convection rolls can result in the addition or removal of a pair of convection rolls in the flow.

One way of understanding this behavior is to consider the stability of convection rolls near onset as a function of their wavelength. A common way of analyzing stability is via a “linear stability” argument. One starts with a motionless state and then assumes a perturbation of a periodic pattern of convection rolls on this motionless state. A growth/decay term is associated with this perturbation, which might be written in the form $A_0 e^{\sigma t} f(k)$, where $f(k)$ is the perturbation with wavenumber k , and σ is the

growth exponent. The growth exponent σ is typically dependent on the value of k (Fig. 5). If $\sigma < 0$ for all values of k , then all perturbations decay, and the motionless state is stable and no convection rolls will develop; this is the case for $Ra < Ra_c$. For $Ra = Ra_c$, $\sigma = 0$ for one particular critical wavenumber k_c ; for Ra just slightly above Ra_c , perturbations with wavenumber k_c should be expected to grow, and, for an infinite system (i.e., no boundaries), a pattern of convection rolls will appear with that precise wavenumber.



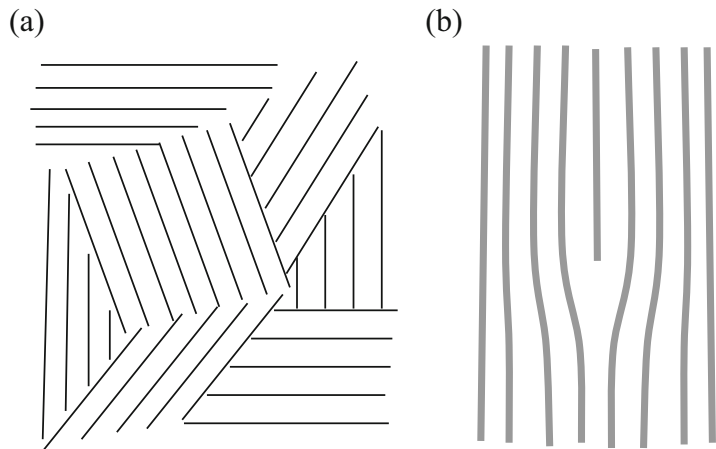
Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 5 Example of a plot of growth exponent σ as a function of wavenumber k , typical of results of linear stability analysis. The bottom curve corresponds to a Reynolds or Rayleigh number below the critical value for instability; σ is negative for all wavenumbers, so all disturbances decay. The middle curve corresponds to the onset of instability. For Ra or Re just above this value, σ is positive for wavenumbers very close to the critical value k_c . For larger Re or Ra (top curve), disturbances over a range wavenumbers are unstable

For $Ra > Ra_c$, there is a range of wavenumbers for which $\sigma > 0$.

The discussion above is idealistic; in realistic systems, boundary conditions have a significant effect on convection patterns. If the fluid layer is confined to a small-to-moderate rectangular box, then the rolls line up parallel to the shortest side of the box, as in Fig. 4. If the width of the box is an integer multiple of the critical wavelength $2\pi/k_c$, then linear stability correctly predicts convection with this wavelength for Ra just barely above Ra_c . If the fluid layer is orders of magnitude wider than the critical wavelength, multiple zones of parallel convection rolls form at random orientation (Fig. 6a); the zones are separated by *grain boundaries*. Over time, some zones grow while others shrink. Ultimately, one zone may end up dominating, with a single pattern of parallel convection rolls covering the entire system.

If contained in a circular container, a pattern of parallel convection rolls cannot be achieved (Heutmacker et al. 1985), because convection rolls tend to line up perpendicular to the side walls. A theory by Swift and Hohenberg (1977) defines a free energy functional – an effective energy that depends on the functional form of the convection pattern; the pattern evolves to minimize this free energy. The free energy is increased by convection rolls that are parallel to the side walls, by bends in convection rolls and by defects in the patterns. Near onset (i.e., for Ra just slightly over Ra_c), a complicated convection pattern forms to minimize this free

Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 6 (a) Sketch of zones of parallel convection rolls separated by grain boundaries. The lines represent boundaries between adjacent rolls, as viewed from above (similar to dashed and dotted lines in Fig. 4). (b) Sketch of a defect in a convection pattern



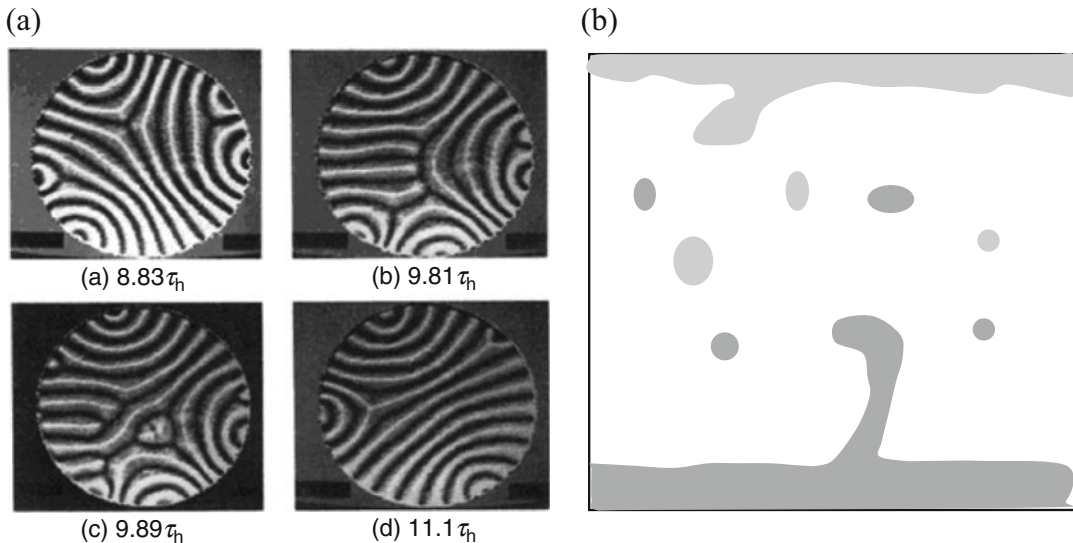
energy functional (Fig. 7a). The patterns that form have local wavenumbers that cannot all be at the critical value k_c ; consequently, the pattern may continually evolve in time, in contradiction to the typical case in which convection with Ra just above Ra_c is time independent.

For large enough Ra , convective flows become turbulent. Two types of turbulent flows are often discussed. At lower (but still large) Ra , complicated convection patterns form with numerous defects. The defects move around significantly in the pattern, resulting in continuous variation in the pattern. This regime is referred to as *weak turbulence* or *defect-mediated turbulence*. For very high Ra , the convection pattern breaks up completely and a regime of *strong turbulence* is found. A side view of convection in the strongly turbulent regime (Fig. 7b) shows that the flow is divided into three regions. Most of the temperature gradient is concentrated into thin boundary layers at the top and bottom of the fluid, while the fluid is well-mixed at roughly the average temperature in the large central region of the flow. The boundary layers are not quiescent; rather, they grow in thickness as heat flows into (for the lower boundary layer) and out of (for the upper

boundary layer) them, eventually becoming unstable and forming plumes that erupt, carrying blobs of warm or cold fluid into the center region. The eruption of these plumes both acts to drive the turbulent flow and also transport heat from the bottom to the top of the system.

Bénard-Marangoni Convection

If a fluid layer with a free surface is heated from below, thermal convection can be driven by variations in surface tension at the surface. This form of convection is referred to as Bénard-Marangoni convection and is usually characterized by a pattern of hexagons. Since the fluid is heated from below, it is unstably stratified. However, the main force driving the flow isn't buoyancy; rather, the flow is driven by gradients in the surface tension at the free surface. An instability occurs in which small variations in the temperature arise on the surface. The surface tension depends on the temperature; consequently, temperature gradients result in surface tension gradients that drive flows along the surface. Regions in which the fluid converges on the surface produce downward-welling flows; upwelling of fluid occurs



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 7 (a) Images of Rayleigh-Bénard convection in a circular container near onset, viewed from above (From Heutmaker et al. 1985). (b) Sketch of

strongly turbulent convection from side, showing the formation of thermal boundary layers at the bottom and top that erupts, sending plumes of hot and cold fluid into the middle region

below regions in which the fluid diverges on the surface.

Transport and Mixing

The manner in which an impurity is mixed within a fluid is an issue with significant practical importance for a wide range of scientific and engineering applications. Mixing of a *passive* impurity (one that follows fluid elements in the flow and whose distribution does not affect the flow itself) is governed by the advection-diffusion equation:

$$\frac{\partial c}{\partial t} = -\vec{u} \cdot \vec{\nabla} c + D \nabla^2 c,$$

where c is a scalar concentration field, $\vec{u}$ is the velocity field, and D is the molecular diffusion coefficient. This equation can be written in non-dimensional form by scaling the velocity field by a characteristic flow velocity U , distance by a characteristic length L , and time by the advection timescale L/U :

$$\frac{\partial c}{\partial t'} = -\vec{u}' \cdot \vec{\nabla}' c + \frac{1}{Pe} \nabla'^2 c$$

where the Peclet number $Pe = UL/D$ characterizes the relative strength of advective to diffusive mixing in the flow. In the limit of no flow ($Pe \rightarrow 0$), mixing is entirely via molecular diffusion caused by Brownian motion of individual tracer particles in the impurity. Molecular diffusion is a slow mixing process; the variance $\sigma^2(t)$ of a distribution grows linearly with time: $\sigma^2(t) = 2Dt$.

The presence of a fluid flow dramatically changes the mixing. An impurity is advected along with fluid elements in the flow but can diffuse away from these deterministic fluid trajectories. Advection of an individual tracer is determined from equations of motion derived from the velocity field $\vec{u} = (u_x, u_y, u_z)$:

$$dx/dt = u_x$$

$$dy/dt = u_y$$

$$dz/dt = u_z.$$

Trajectories are determined by integrating these equations of motion. If the flow is two-

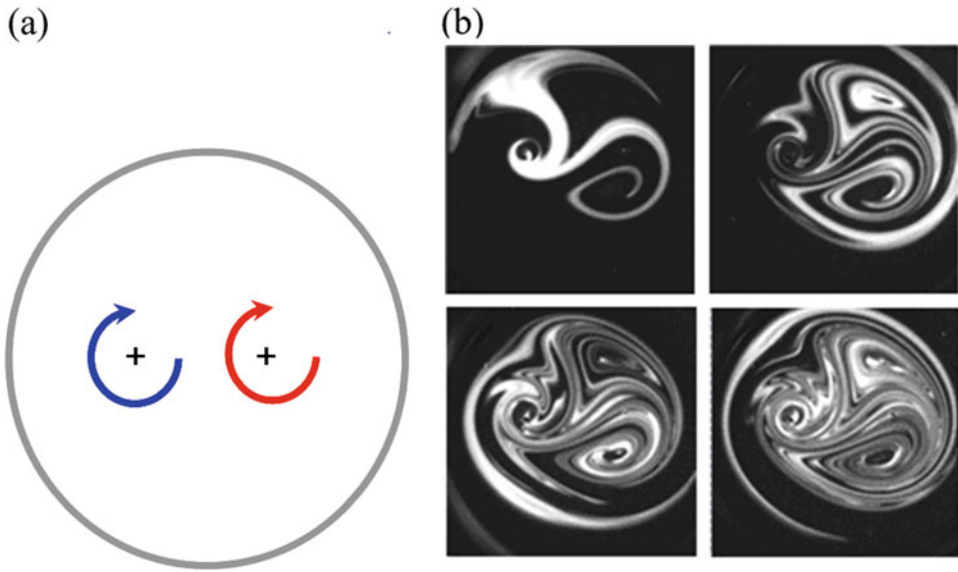
dimensional and time-independent ($\vec{u} = \vec{u}(x, y)$ and $u_z = 0$), then tracer trajectories are *integrable* (well-ordered). For two-dimensional, time-periodic or three-dimensional, time-independent flows, however, the equations of motion in general are not integrable, and trajectories are often chaotic, with nearby tracers separating roughly exponentially in time (sensitive dependence on initial conditions).

The most well-known flow exhibiting *chaotic advection* is the blinking vortex flow proposed by Hassan Aref (1984). The flow is shown in Fig. 8a; the fluid alternates periodically between circling around the left vortex and around the right vortex. Advection of a blob of a passive dye is shown in Fig. 8b (Nugent et al. 2004). Mixing is associated with a repeated process of stretching and folding of tendrils of the impurity. Stretching and folding behavior such as this is typical of chaotic mixing.

Transport on scales larger than typical length scales of flow can be illustrated with the alternating vortex chain (Solomon and Gollub 1988) shown in Fig. 9. If the (two-dimensional) flow is time independent, tracers follow ordered and closed trajectories within individual vortices. The presence of molecular diffusion allows for tracers to diffuse from one vortex to the next. The combination of advection around and diffusion between the vortices results in enhanced transport whose variance grows linearly in time: $\sigma^2(t) = 2D^*t$, where D^* is the *enhanced diffusion coefficient*.

The simplest time dependence for the alternating vortex chain is a simple lateral oscillation of the entire chain, similar to time dependence found in Taylor-Couette and Rayleigh-Bénard flows for intermediate values of Re and Ra . A passive tracer moving in this flow circles around an individual vortex, but if it is near a separatrix (boundary) between vortices, it can cross between vortices. Over time, the tracer alternates between circling within and crossing between vortices in an erratic manner. The trajectories are rigorously chaotic in the sense that nearby trajectories separate roughly exponential as a function of time.

Not all tracers in the flow follow chaotic trajectories. Tracers near the center of a vortex remain trapped within that vortex, following a trajectory that is well-ordered and *not* sensitive



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 8 (a) Sketch of blinking vortex flow. Fluid alternates between circling around left and right

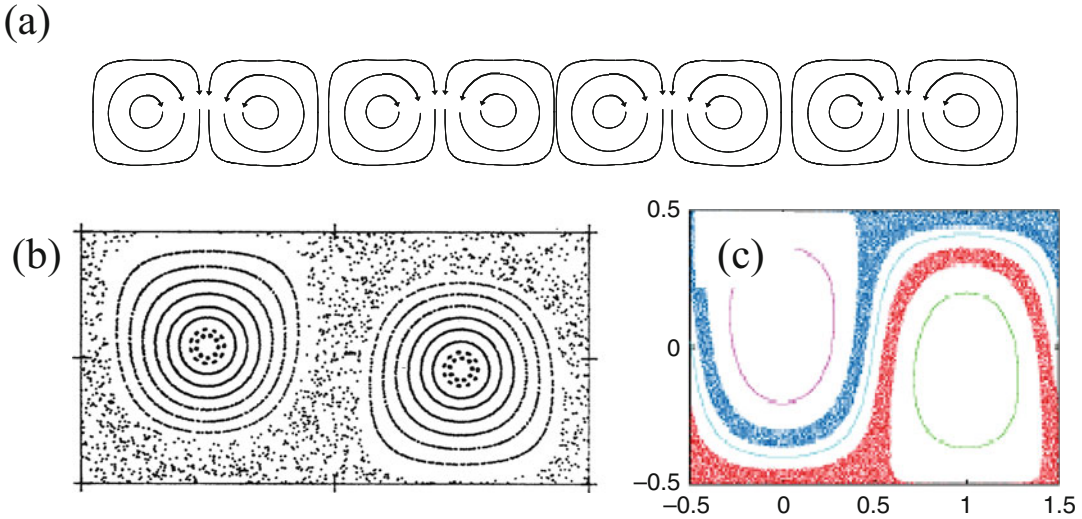
vortex centers. (b) Mixing of dye in blinking vortex flow. Images are separated in time by one period of oscillation each. (From Nugent et al. 2004)

to initial conditions. The separation of the system into both ordered and chaotic regions of transport can be seen easily by plotting a *Poincaré section* (Fig. 9b), a plot that shows the location of one tracer (or more) once every period of the flow. A tracer that starts in the chaotic region will eventually explore the entire chaotic region, which shows up on the Poincaré section as a pattern of dots. A chaotic trajectory can never cross into a region with ordered trajectories; consequently, the ordered regions show up as white “islands” on a Poincaré section.

The boundaries between ordered and chaotic regions – referred to as *Kolmogorov-Arnold-Moser (KAM) invariant surfaces* – act as barriers against transport and mixing in the flow. KAM barriers are very common in laminar flows and also show up in many flows found in nature, even turbulent ones. Examples of transport barriers include the ozone hole over Antarctica, Gulf stream rings in the Atlantic Ocean, and coherent vortices (called *meddies*) originating in the Mediterranean Sea that cross the Atlantic and maintain the salinity and biological constituency found in the Mediterranean for months and even years. Another well-known example of a transport barrier is the Great Red Spot of Jupiter, a large

coherent patch of vorticity in a very turbulent atmosphere that clearly acts as a transport barrier, evidenced by the fact that it has maintained its distinct color for centuries.

Chaotic advection results in significant enhancements in long-range transport. In many cases, enhanced transport is diffusive with a variance that grows linearly in time. However, *anomalous diffusion* is also possible where the variance grows as a power law in time with a growth exponent different from 1: $\sigma^2(t) \sim t^\gamma$ with $\gamma \neq 1$. Transport with $\gamma < 1$ is called *subdiffusion* and transport with $\gamma > 1$ is called *superdiffusion*. The presence of islands of ordered trajectories is often associated with subdiffusive transport; tracers in the chaotic region stick to the outside of these islands and possibly diffuse inward due to Brownian motion. Superdiffusion is associated with *Lévy flight* trajectories where tracers jump large distances between regions in the flow. An example of a flow with superdiffusion is the alternating vortex chain with both oscillatory and drifting time dependence (Paoletti et al. 2006) (Fig. 9a). A Poincaré section for transport in this flow is shown in Fig. 9c. Two distinct chaotic regions are apparent, and in addition to ordered islands in the vortices, there is also a snake-like



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 9 (a) Sketch of alternating vortex chain. (b) Poincaré section for oscillating vortex chain, showing ordered regions of transport in vortex cores and

chaotic region around and between vortices. (c) Poincaré section for oscillating and drifting vortex chain. (From Paoletti et al. 2006)

region of ordered trajectories that wind around the vortices. A tracer in the chaotic region in this flow alternately sticks to islands (remaining temporarily confined to a vortex) and to the snake region (traveling rapidly along the vortex chain).

Chaotic advection is also possible in three-dimensional flows, even those that are time independent. An example of such a flow is shown in Fig. 10 – a chain of alternating vortices superposed with a second chain which is shifted by half of a vortex width and is oriented with its vortex axes perpendicular to those of the first chain (Fogleman et al. 2001). Trajectories of tracers in this flow are shown in Fig. 10b. A Poincaré section (Fig. 10c) again shows coexistence of both ordered and chaotic regions of transport in the flow.

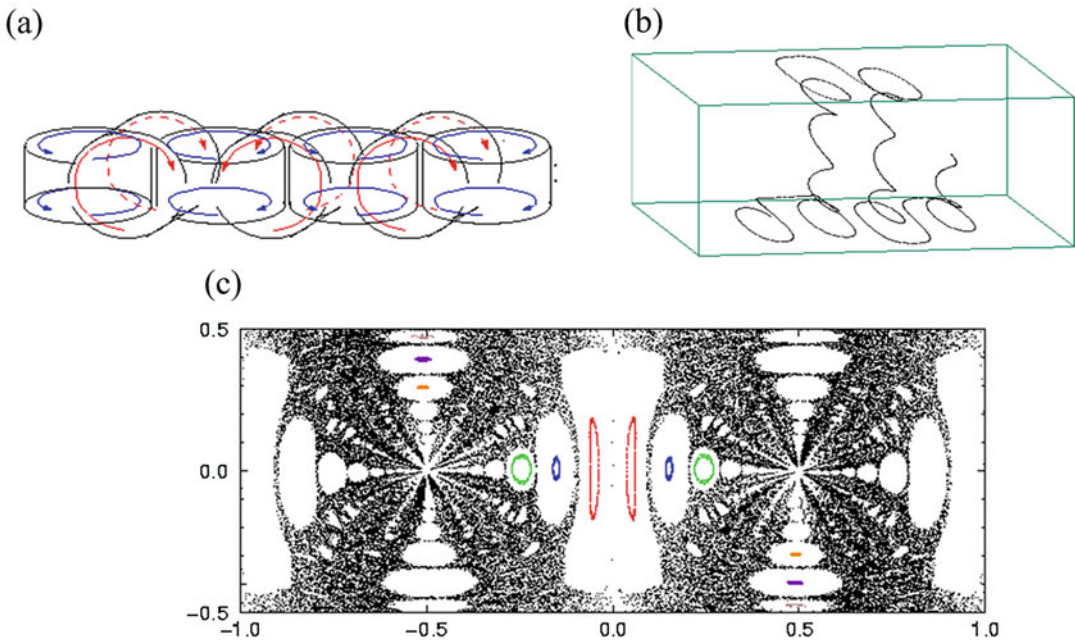
There are numerous applications of chaotic mixing. Chemical engineers have already begun to develop and market devices that take advantage of chaos to enhance mixing in low-Reynolds number flows. Chaotic mixing is particularly useful for mixing of high-viscosity fluids for which turbulent mixing would be difficult and/or tremendously expensive energetically. Chaotic mixing is also finding significant applications in the expanding field of microfluidic devices,

so-called factories-on-a-chip, again which involve very small Reynolds numbers due to the small length scales of these systems.

Manifolds, Lobes, and Transport Barriers

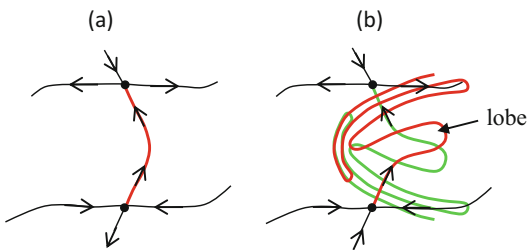
In addition to KAM invariant surfaces, transport barriers can also be found associated with *invariant manifolds* in the system. Manifolds are found connected to fixed points in the flow, as shown in Fig. 11. In general, an invariant manifold is a set of points in the flow that map onto themselves when integrated forward in time. For passive transport, an *unstable manifold* of a particular fixed (stagnation) point in the flow can be determined conceptually by starting with a large number of passive tracers, initially infinitesimally close to the fixed point. The locations of these tracers at a distant time in the future are the *unstable manifold* of that fixed point. Similarly, the *stable manifold* of a fixed point is the locations of tracers that will converge on the fixed point in the distant future.

For a time-independent, two-dimensional flow, the unstable manifold of one fixed point often coincides with the stable manifold of a



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 10 (a) Sketch of time-independent, nested vortex chain flow. (b) Example of a

chaotic trajectory for the nested vortex flow. (c) Poincaré section at the mid-height of the flow, showing both ordered and chaotic regions. (From Fogleman et al. 2001)



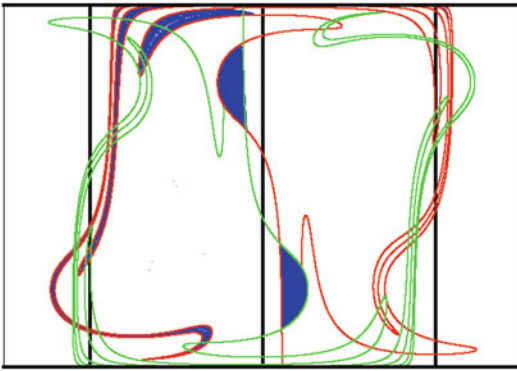
Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 11 Stable and unstable manifolds of two hyperbolic fixed points in a flow. (a) Time-independent flow; the unstable manifold (in red) of the lower fixed point is the same as the stable manifold of the upper fixed point. (b) Time-periodic flow; the unstable manifold (red) of the bottom fixed point undulates, as does the stable manifold (green) of the upper fixed point

neighboring fixed point, as shown in red in (Fig. 11a). This manifold acts as a transport barrier, with passive impurities on one side staying on that side. But the unstable and stable manifolds often separate – and become very complicated – if the flow is time dependent, even for periodic time dependence, as shown in (Fig. 11b). The

manifolds in this case are still transport barriers, but since the flow is time dependent, the manifolds themselves undulate in time, and the tracers can move through the flow with the moving manifolds. The regions surrounded by pieces of overlapping stable and unstable manifolds are referred to as “lobes” (or “turnstile”) (Solomon and Gollub 1988; Camassa and Wiggins 1991; Rom-Kedar and Wiggins 1991).

The lobes form a mechanism by which tracers can be transported between different regions in the flow. This is best illustrated with the alternating vortex flow (Fig. 9a and Fig. 12). Impurities trapped in a lobe can’t escape the lobe. But as the manifolds undulate periodically, the lobes move such that the first lobe (to the right of the middle black line) maps to second lobe (immediately to the left of the middle black line) after one oscillation period, then to third lobe after two periods, etc. Consequently, impurities initially in the first lobe move from one vortex to another. This results in long-range transport in the vortex chain (Solomon and Gollub 1988; Camassa and Wiggins 1991)

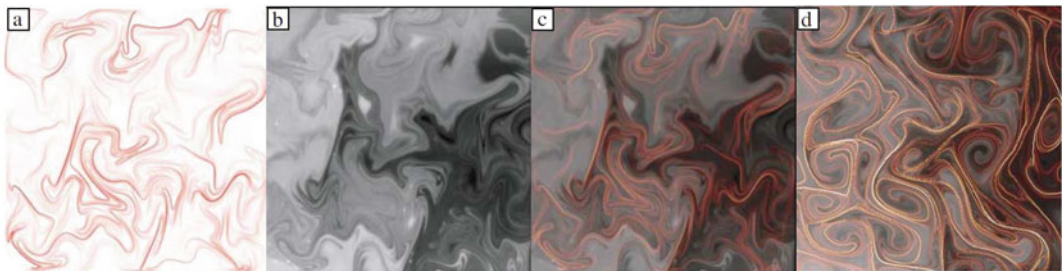
Recently, the manifold picture has been extended to more complicated, time-a-periodic flows. Several groups have investigated what are now called *Lagrangian coherent structures (LCS)* (Haller 2015), which are generally defined as regions in a flow where passive tracers are advected together. For instance, tracers in the Great Red Spot of Jupiter remain together – and have so for hundreds of years, indicated by the fact that it has remained red in color – even though the vortex flow of the Spot is embedded within a very turbulent flow.



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 12 Stable and unstable manifolds of the hyperbolic fixed points for the alternating vortex chain. The straight vertical lines are the separatrices between adjacent vortices and are also the manifolds for the time-independent case with no lateral oscillations. The complicated (stretched and folded) manifolds correspond to time-periodic, lateral oscillations of the vortex chain. Some of the lobes formed from the intersections of these manifolds are shaded in

But LCS approaches also identify manifold-like structures in 2D fluid flows, even if the flow is aperiodic and even weakly turbulent. The most common approach is to calculate finite-time Lyapunov exponent (FTLE) – or *stretching* – fields for the flow (Voth et al. 2002; Mathur et al. 2007). The *ridges* in the field that follow local maxima in the FTLE have sometimes been identified as *repelling LCS* and ridges in the backward-time FTLE fields as *attracting LCS*. These structures have been identified as local barriers for the mixing of passive impurities, similar to (and equivalent in the time-independent limit) unstable and stable manifolds, as seen in the experimental images from Voth et al. (2002) in Fig. 13.

There have been numerous studies of Lagrangian coherent structures since the first papers in the early 2000s. Follow-up studies have argued that FTLE ridges may not be the best indicator of repelling and attracting LCS and that instead a variational approach (Haller 2011) would do a better job. Several groups have proposed alternate approaches for detecting coherent transport structures, including approaches involving ergodic partition (Mezić and Wiggins 1999), maps of mesohyperbolicity and mesoellipticity (Mezić et al. 2010), almost-invariant sets (Froyland and Padberg 2009), an *M-function* (Mendoza and Mancho 2010) that identifies *distinguished trajectories* that separates the system into regions of qualitatively different types of trajectories, and *shape coherence* (Ma and Bolit 2014) based on time evolution of curvature of boundary curves. Concurrently with the development of these



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 13 (a) Stretching fields calculated from a 2D flow. (b) Evolving dye concentration in the same flow. (c) Superposition of stretching fields from (a) and dye

concentration profile from (b). (d) Superposition of dye concentration field and time-reversed stretching fields. (From Voth et al. 2002)

approaches, other groups have focused on developing techniques for the identification of coherent transport structures from experimentally sparse data such as that obtained by a finite number of ocean floats. These sparse data approaches are based on topological arguments and involve identification of *braiding patterns* (Thiffeault and Finn 2006) and the evolution of stretching “rubber bands” advected by the flow (Roberts et al. 2019).

Other research groups have extended LCS approaches to a wider range of transport problems involving impurities that aren’t necessarily passive (Balasuriya et al. 2018).

Pattern Formation in Reaction-Diffusion and Advection-Reaction-Diffusion Systems

Another class of nonlinear, pattern-forming systems is the well-known reaction-diffusion (RD) problem. The reaction is a process in which one or more species somehow changes into something different. Examples include chemical reactions, biological interactions of some sort (such as the interaction of a disease with a population of people or animals or a predator-prey system), and a wide range of phase transitions. In an extended, nonflowing system, the reaction typically occurs at different times in different locations in the system, resulting in the formation of patterns. The key to the formation of these patterns is the interaction between the reaction at local regions in the system and molecular diffusion which (for a nonflowing system) is the only means of communication between different regions.

A general form of the RD equation can be written as follows:

$$\frac{\partial c}{\partial t} = f(c) + D\nabla^2 c$$

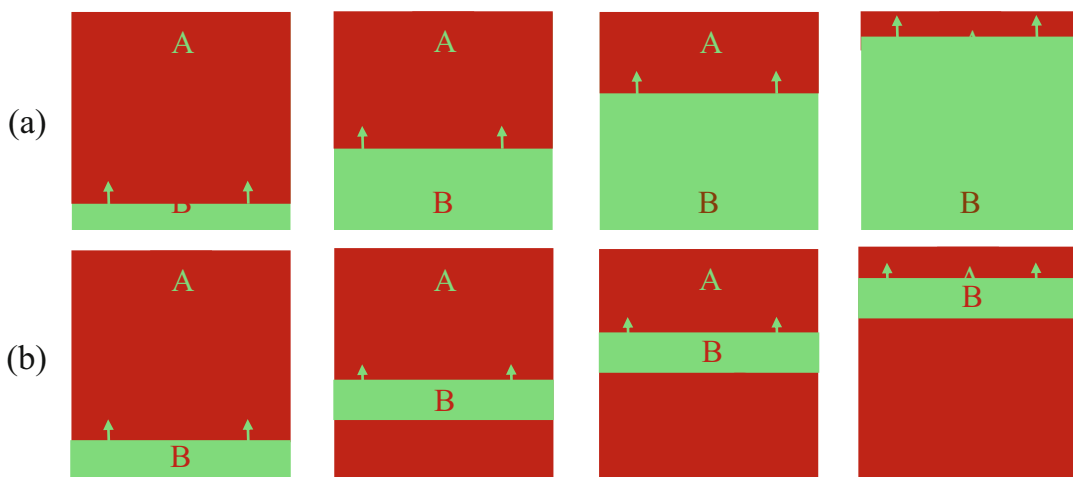
where c is a concentration field of some chemical, biological, or physical species, and the first term on the right denotes some sort of reaction. The details of the reaction term itself vary from system to system; however, some common behavior is

found in a wide range of RD systems, independent of the details of this reaction term.

The field of reaction-diffusion studies was enhanced significantly by the discovery of the oscillatory *Belousov-Zhabotinsky* (BZ) chemical reaction. Discovered in the 1950s, this reaction is well-known to have a pH that oscillates for hours when well-mixed in a beaker or a flask. When catalyzed with a pH-indicator such as ferroin, the chemicals can be observed to alternate back and forth between a red and blue color during this period before the reaction finally runs down. The oscillation is typically nearly periodic, but conditions have been found in which chaotic oscillations can be found in the BZ reaction.

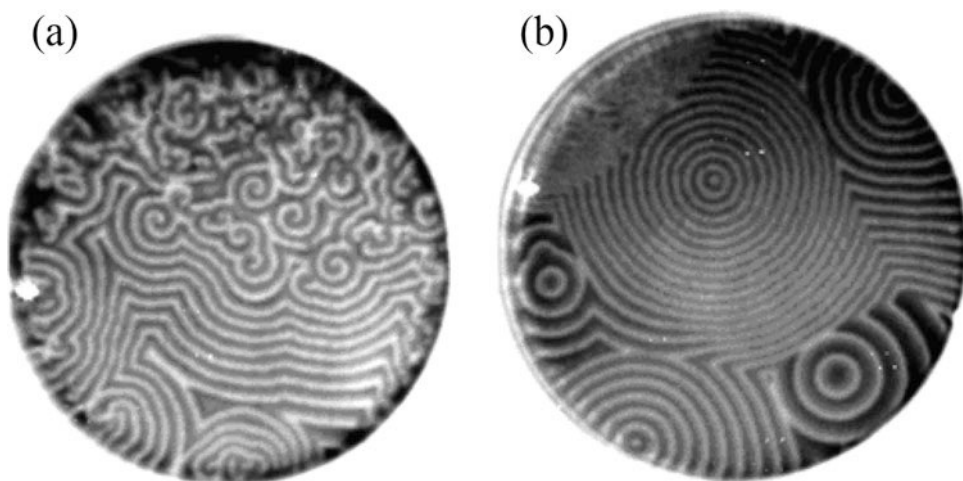
Reaction-diffusion systems can also produce propagating fronts if the reaction is a one-shot (or “burn”) reaction (i.e., $A \rightarrow B$) or if the reaction is *excitable*, as shown in Fig. 14. An excitable reaction is one in which some trigger turns species A into B, but then the system slowly resets back to state A after a *refractory* timescale. A forest fire is an example of a one-shot reaction, unless the trees grow back *really* (unreasonably) fast. The BZ reaction has an excitable regime in which it forms pulse-like reaction fronts. A nerve pulse is also excitable – a trigger causes the nerve to fire, and there is a refractory period after the firing during which the potential in the nerve resets. After the refractory period, the nerve can be triggered to fire again.

A one-shot reaction in a spatially extended system produces a *burn-like* front, as sketched in Fig. 14a, whereas a spatially extended excitable system produces pulse-like reactions (Fig. 14b). Depending on the nature of the trigger, excitable systems can also produce patterns called *trigger waves*. For example, if the chemicals for the excitable BZ reaction are in a shallow petri dish with no flow (or in a gel or fritted disk that inhibits a flow), spiral and/or target patterns form, as seen in Fig. 15. Patterns similar to these have been observed in a wide range of physical, chemical and biological systems. Examples include (a) spiral waves of electrical activity in the heart which act as pacemakers; breakdown of these spiral waves are associated with cardiac fibrillation; (b) spiral waves of “spreading depression” in



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 14 (a) Reaction front for a one-shot (or "burn") reaction where species A turns into species B. (b) Reaction front for an excitable reaction where

species A turns into species B and then back into A after a refractory period. Fronts in excitable systems are typically pulse-like fronts



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 15 Examples of reaction-diffusion patterns formed by the Belousov-Zhabotinsky chemical reaction in a thin layer in a petri dish

the brain that are associated with migraine headaches; (c) spiral patterns found in developing embryos which may be partially responsible for morphogenesis in which different cells in the embryo develop different roles in the growing organism; and (d) spiral and target patterns in populations of slime molds in a stagnant system. Because of the similarity of these patterns to those found in the BZ system, there has been a significant amount of research into the properties of the

BZ system, which is considered to be a paradigm of RD systems. Reaction-diffusion dynamics also explain the propagation of fronts in stagnant systems, e.g., the spreading of a fire in the absence of any winds or the growth of a solid in the absence of fluid flows.

In both natural and industrial systems, reacting systems are rarely stagnant; flows dramatically affect the mixing and therefore the communication between different parts of the system. The

more general *advection-reaction-diffusion* (ARD) problem is represented by the following equation:

$$\frac{\partial c}{\partial t} = -\vec{u} \cdot \vec{\nabla} c + f(c) + D\nabla^2 c$$

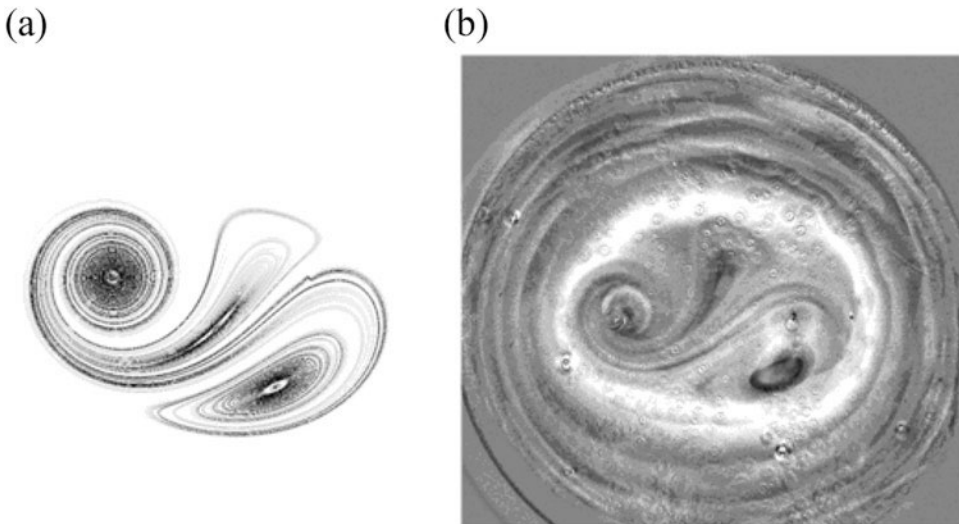
where the additional term on the right denotes advection of the relevant species by the fluid flow. Advection-reaction-diffusion dynamics are relevant for pattern formation and front propagation in a wide range of systems, including marine ecological systems (e.g., algae and phytoplankton blooms), microfluidic chemical and biological processing and diagnostics, forest fires in the presence of winds, and the propagation of disease in a moving population.

If the mixing is chaotic, it has been shown (Tel et al. 2005) that ARD patterns reflect the structures that characterize chaotic mixing in the flow. An example (Nugent et al. 2004) is the BZ reaction in a blinking vortex flow (Fig. 8), in which fluid circulates alternately (and periodically) between two separate vortex centers. As seen in Fig. 16, except for very weak mixing, the patterns associated with chaotic mixing end up dominating the pattern formation process for the ARD system as well (Nugent et al. 2004). Ideas such as this have been used to explain patterns of populations

of marine organisms in both the Gulf of Mexico and in the northern Atlantic Ocean.

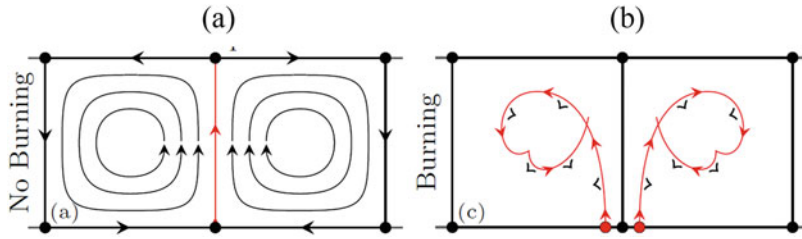
Burning Invariant Manifolds and Reaction Fronts

The manifold theory described in section “[Manifolds, Lobes and Transport Barriers](#)” can be extended to describe front propagation in advection-reaction-diffusion systems. We can use the alternating vortex chain flow to explain the behavior. Figure 17 shows two adjacent vortices in the time-independent, alternating chain vortex flow. For passive mixing, there are fixed points in the flow (black dots in Fig. 17) – where the fluid velocity is zero – and manifolds (red curve) that connect the fixed points. If the fluid is the medium for a one-shot or excitable reaction, then if a reaction is triggered at the bottom center fixed point, a reaction front will propagate outward from that point. Of course, the front will propagate upward along the direction of the unstable passive manifold since the fluid velocity is upward in that region. But the reaction can also propagate leftward and rightward against the incoming flow. But since the incoming flow increases with



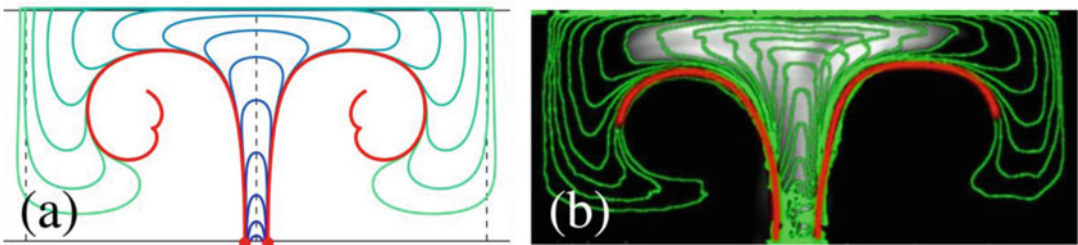
Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 16 (a) Simulation of mixing field for blinking vortex flow. (b) Advection-reaction-

diffusion pattern for Belousov-Zhabotinsky chemical reaction in the same flow. (From Nugent et al. 2004)



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 17 (a) Fixed points (black dots) and passive invariant manifold (red curve) for passive mixing in two side-by-side alternating vortices. (b)

Burning fixed points (red dots) and burning invariant manifolds for reaction front propagation in the same flow. The black carrots indicate the local blocking direction for the BIMs. (From Mahoney et al. 2012)



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 18 (a) Simulation of burning variant manifolds (red curves) and contours of a propagating reaction front (blue to green curves) triggered initially at

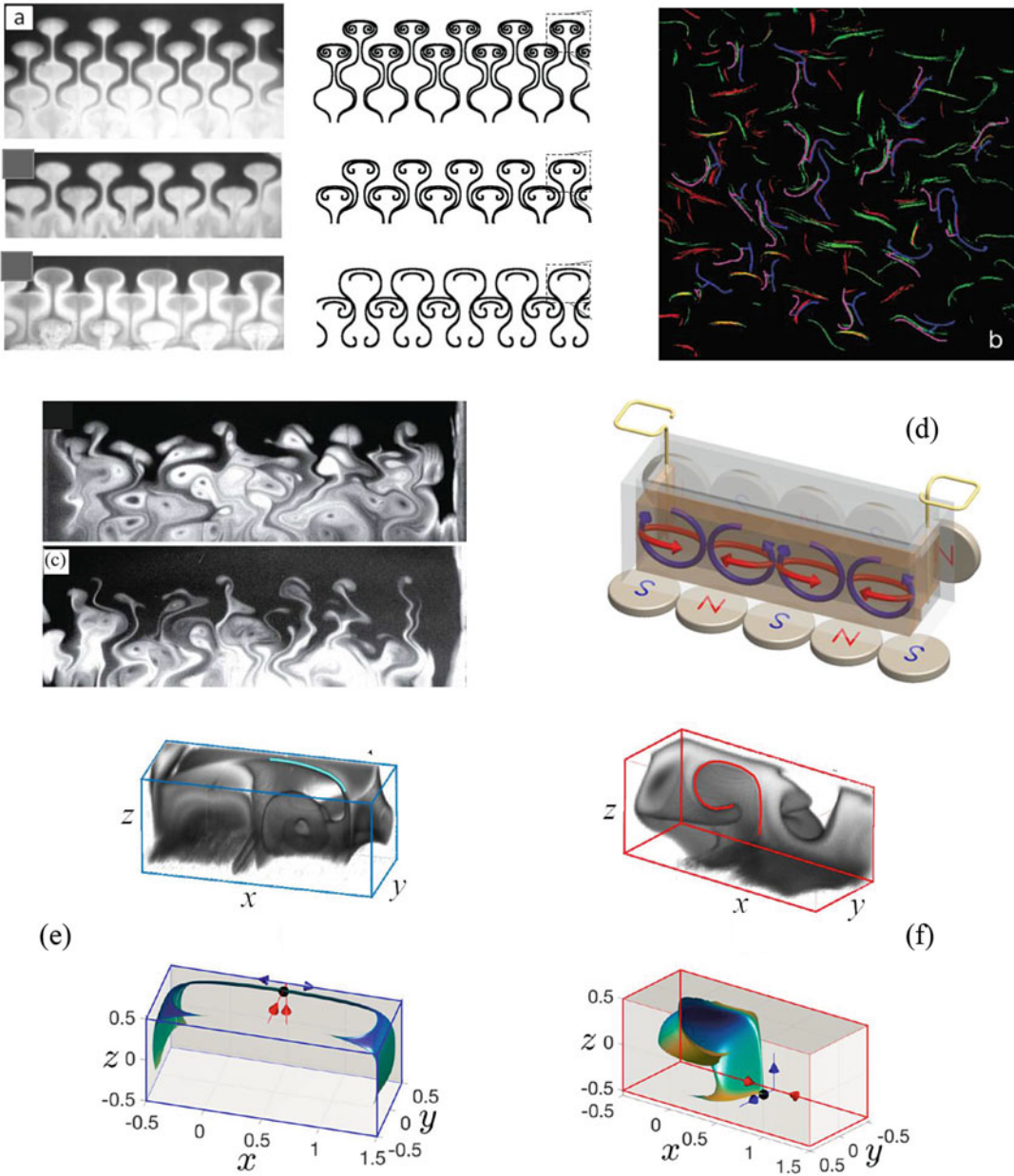
the bottom/center stagnation point. (b) Experiments showing front contours and inferred BIMs for the same flow. (From Mahoney et al. 2012)

distance from the fixed point, the reaction front eventually reaches a point where the incoming flow speed and the outgoing reacting speed are the same; at that point – referred to as a *burning fixed point* (red circles in Fig. 17) – the reaction stops. And as there are passive manifolds attached to passive fixed points in the flow, there are *burning invariant manifolds (BIMs)* (Mahoney et al. 2012; Bargteil and Solomon 2012; Mitchell and Mahoney 2012) attached to the burning fixed points.

Like the passive invariant manifolds, the BIMs act as barriers, with these barriers blocking propagating reaction fronts rather than passive impurities. Unlike the passive manifolds, however, the BIMs block reactions in one direction only. To understand this one-way behavior, imagine triggering a reaction on the bottom edge of the flow in Fig. 17, to the left of the left burning fixed point. That reaction can

propagate to the right, and when it reaches the left burning fixed point and BIM, it passes right through since the flow and the reaction are both going to the right. If a reaction front is triggered at the passive fixed point, however, it is blocked by both BIMs in Fig. 17. The result is a reaction that propagates upward between the two BIMs (as shown in Fig. 18), penetrating into the vortex centers only after it reaches cusps in the BIMs that signify a reversal in the blocking direction.

The ability of BIMs to act as one-way barriers has been demonstrated experimentally for a range of two- and three-dimensional fluid flows. One of these experiments is shown in Fig. 18b for the alternating vortex flow (Mahoney et al. 2012; Bargteil and Solomon 2012). Other examples are shown in Fig. 19, including reaction barriers that produce stationary fronts in 2D vortex array flows with imposed winds (Megson et al. 2015) (Fig. 19a); a



Nonlinear Fluid Flow, Pattern Formation, Mixing, and Turbulence, Fig. 19 Experimental evidence of burning invariant manifolds in laminar flows. (a) Experiments (left) and predicted BIMs (right) for reaction in a 2D vortex array flow with imposed wind. (From Megson et al. 2015). (b) Measured barriers (red and green) and predicted BIMs (purple) for spatially disordered, 2D flow (From Bargteil and Solomon 2012). (c) Stationary reaction

patterns for spatially disordered 2D flow with imposed wind (From Megson et al. 2015). (d) Time-independent, 3D flow composed of superposed horizontal (red) and vertical (blue) vortex chains (From Doan et al. 2018). (e) and (f) experimental (top) reaction front barriers and predicted BIMs (bottom) for 3D flow shown in (d). (From Doan et al. 2018)

spatially random 2D flow (Bargteil and Solomon 2012) characterized by multiple BIM segments (Fig. 19b); a random flow with an imposed wind (Megson et al. 2015) that produces stationary fronts with surprisingly complicated shapes, again, determined by BIMs in the system (Fig. 19c); and a 3D flow (Doan et al. 2018) (Fig. 19d) composed of the superposition of a vertical and horizontal vortex chain that produces tube-like (Fig. 19e) and sheet-like barriers (Fig. 19f).

Other Examples of Pattern-Forming Systems

Patterns similar to those discussed above are found in a wide range of systems spanning all fields of science and engineering. Some examples are as follows:

- Electrohydrodynamic convection in flows of nematic liquid crystals.
- Wave patterns on the surface of a fluid oscillated periodically in the vertical direction.
- Vibrating granular systems
- Bubble froths
- Ferrofluids – labyrinth patterns

This is just a small sample of the many nonlinear, pattern-forming systems that have been studied during the past few decades.

Future Directions

The study of nonlinear systems is an ongoing and continually evolving field. Nonlinear dynamics span a wide range of fields of study, including all of the fields of sciences and engineering, as well as mathematics, medicine, economics and even some fields of social sciences. Not only are there numerous ongoing studies of the basic mathematical and scientific behavior of nonlinear systems, but there are also many applications that are being developed, based on the principles of nonlinear systems.

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Fluid Dynamics in Clouds

The Sum of Its Parts

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Article Outline

Glossary
Why Study Clouds
Definition of the Subject
Microphysics Without Thermodynamics
Microphysics with Thermodynamics
Conclusion and Future Directions
Bibliography

This entry is aimed at describing cloud physics with an emphasis on fluid dynamics. As is inevitable for a review of an enormously complicated problem, it is highly selective and reflects of the authors' focus. The range of scales involved and the relevant physics at each scale are described.

Particular attention is given to droplet dynamics and growth, and turbulence with and without thermodynamics.

Glossary

Aerosol: Tiny (~ 0.1 – 1μ) solid particles suspended in the air. There are about 100–1000 aerosol particles per cubic centimeter of air.

Clouds: Mixtures of air ($\sim 99\%$ by weight), water vapor (1%), liquid water droplets (0.1%), aerosol particles, trace gases. Clouds are usually in turbulent flow.

Caustics: Regions of the flow where particles with different velocities arrive simultaneously at the same location.

Supersaturation: A system that has more water vapor than the saturation value prescribed by the Clausius-Clapeyron equation 5.

Ventilation effects: The effects of oncoming flow on the growth of droplets. Used in the context of water droplets growing by condensation.

Why Study Clouds

Clouds, since they involve many different phenomena interacting with each other in complex ways, are of interest purely from scientific curiosity. For instance, is it possible to predict what cloud shapes will result for given atmospheric conditions? More importantly, perhaps, clouds are also immensely influential in the energy and mass balances in the planet's atmosphere. In fact, clouds are the last great sources of uncertainty in climate science.

For instance, clouds increase the planet's albedo, reflecting away sunlight before it can make it to the surface; they also act to provide a greenhouse effect, trapping energy radiated away from the surface. These two opposing effects are both of much larger magnitudes than any other sources in the radiative balance of the planet (Archer 2011, Chap. 6; Stevens 2013). The response of clouds to a warming planet – whether clouds will act to slow down or to accelerate the planet's warming – is not clear at present (although very recent studies (Schneider et al. 2019) suggest that they do indeed act as positive feedback). This uncertainty is due to the large magnitudes of the aforementioned effects and the fact that clouds are coupled with the global circulation.

Similarly, the selective annual Northward propagation of the cloud-band known as the ITCZ (Inter-Tropical Convergence Zone) over longitudes including those of the Indian landmass brings the Indian monsoon, among the biggest weather events, which provides fresh water for close to two billion people. Understanding the dynamics of the ITCZ requires understanding the dynamics of clouds, which is as yet an open problem (Bony et al. 2015). These are only a few of the most compelling reasons to study clouds.

With the advent of machine learning and associated statistical and data-driven techniques, and the increasing availability of dedicated computing power, it is tempting to rely solely on such statistical methods. However, understanding the dynamics is useful not just as a scientific exercise but also pragmatically. Statistical techniques – machine learning in particular – are best used in scenarios for which they have been “trained.” Most estimates suggest that the feedback from clouds on the climate is likely to affect the circulation in the atmosphere substantially. The resulting large changes in the dynamics may not be possible to capture with machine learning techniques. The planet needs us to study the dynamics of clouds! (Schiermeier 2015).

Definition of the Subject

The fluid dynamics in clouds covers length scales from tenths of microns to hundreds of kilometers. Being a nonlinear problem, the physics at each scale has an effect on other scales. There are open questions that require an understanding of the basic physics at each scale, and also in the connections between scales. The lower end of this range concerns the chemistry and chemical physics of aerosols. Aerosols are crucial to cloud formation, because they act as nuclei for droplet formation, as will be discussed below. Aerosols are introduced into the atmosphere in a variety of ways, natural and anthropogenic. The production of aerosols, especially sea-salt aerosol by the mechanics of wave-breaking at the surface of the ocean, is an outstanding problem of fluid mechanics. The upper end of the range of length scales

covers the dynamics of weather and the climate. Significant progress has been made in recent years, aided by advances in supercomputing, in the ability to make reasonable predictions of the dynamics on these scales. The robustness of these predictions depends, however, on understanding the global dynamics at the “sub-grid scales.” The intermediate range, incorporating the interactions of buoyancy-driven fluid turbulence of (dilute) suspensions, is not only exceedingly complex, but also controls the dynamics of processes at the largest scales related to weather and climate. We will describe recent progress in understanding the dynamics in the intermediate length scales.

Studies of the cloud dynamics can be based on observations of clouds either in the real world or in the laboratory, or on analyses or numerical solutions of the fluid dynamical equations of motion. Our work is in the latter, and we will for the most part restrict ourselves to discussing theoretical/numerical studies of clouds, although we do make note of some relevant experimental studies.

An important ingredient in the intermediate scales is that clouds are usually in turbulent flow. Turbulence consists of vortices and regions of shear whose length scales span a large range, starting from the biggest scale in a single cloud, of the order of a few kilometers, to what is known as the Kolmogorov scale η , which is of the order of a millimeter in a cloud. A turbulent flow is characterized, among other properties, by its Reynolds number, which is a ratio of inertial and viscous forces. Consider a cloud of length scale $L \sim 1$ km in height and width, where velocities U are of the order of 10 m/s. The kinematic viscosity ν of air is about 10^{-5} m²/s. The Reynolds number is $LU/\nu \sim 10^9$.

The range of length scales involved even within the intermediate range in clouds is vast. Accurate direct numerical simulations (DNSs), solving the Navier-Stokes equations or their variants, have to resolve the Kolmogorov scales of turbulence. If these scales have to be resolved in simulations of a cloud of the length scale of 100 m, each dimension has to be resolved with $O(10^5)$ grid points. Such numerical simulations are impossible with today’s computing resources.

DNSs of cloud flows are typically conducted only within small boxes, of a few meters in length (Kumar et al. 2012, 2013, 2014). In other words a small volume within a cloud is all we can simulate. In effect experiments (on a computer or in the laboratory) can be performed at Reynolds numbers that are much smaller than those found in clouds, in the hope that this will nevertheless provide useful answers (Abma et al. 2013; de Lozar and Mellado 2013, 2015, 2017; Pauluis et al. 2010; Schumacher and Pauluis 2010; Weidauer et al. 2010; Pauluis and Schumacher 2011; Narasimha et al. 2011; Ravichandran and Narasimha 2020) at cloud Reynolds numbers (see also section “[Cumulus Clouds: Phase-Change+Buoyancy+Turbulence](#)”). Workarounds for this limitation take the form of large eddy simulations (LESs) which resolve only the large scales of motion (i.e., they are “cloud-resolving”) (Randall et al. 2003; Jarecka et al. 2009; Roms 2010; Grabowski 2014) and use models to account for the smaller scales including the microphysics of phase-change.

Even simulations that resolve the Kolmogorov scales of the flow cannot resolve the scales associated with the motion of the water droplets in clouds, which range from about a micron to a few millimeters. Even the simplest approach to tracking droplets adds significantly to the burden of computations, given that there are $O(1000)$ small droplets per cubic centimeter of cloud. In the simplest approach, the finite-sized water droplets have to be treated as point particles and tracked in a Lagrangian sense. Alternatively, these particles can be coarse-grained into a field. The relative efficacies of these two approaches to particle-dynamics are studied in Mitra and Perlekar (2018). The effects of finite droplet size and how this changes their dynamics is discussed at length in section “[Microphysics Without Thermodynamics](#).” These are known as “one-way coupled” approaches, where the fluid equations are solved for without taking into account the fact that fluid is carrying particles and droplets, whereas the dynamics of the particles and droplets are dictated by the fluid motion. For a dilute suspension of small particles and droplets this is a fair approach. However, larger raindrops can

affect the flow and can affect the dynamics of each other, and a perfect treatment would have to account for the forces of these objects on the fluid and on each other (two-way or four-way coupling). This can make computational costs forbidding.

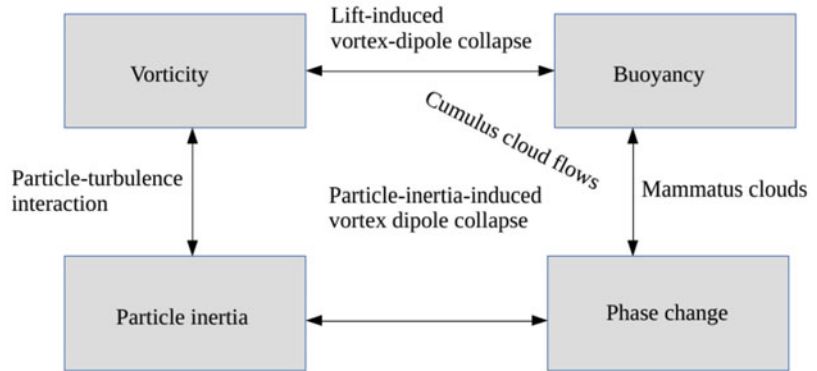
The thermodynamics taking place within a cloud has an important effect on the dynamics. Phase change results in heat release, which results in buoyancy. The potential energy thus gained is converted into the kinetic energy of turbulence. Thus turbulence in a cloud is fundamentally different from mechanically forced turbulence, and turbulence from heat supplied at the boundaries, which are studied most often. We return to this point in section “[Thermodynamics of Phase-Change](#).” The droplet-growth bottleneck is a well-known open problem. Droplets can grow quickly to about $10\ \mu$ in size in a supersaturated environment typical of clouds. Once they are about $50\ \mu$ in diameter, gravity can aid in the process of droplet growth by enhancing collision probability, with some fraction of all collisions resulting in coalescence. How droplets grow from about 10 to about $50\ \mu$ is not completely understood yet, and this is known as the droplet-growth bottleneck. Turbulence is widely accepted now to be a big part of the answer, and this is discussed below.

Most present-day studies assume that water droplets are spherical in shape whereas larger drops are sensitive to gravity and can distort in shape from the spherical, even to the point where they adopt shapes which are locally sheet-like, which then causes breakup into smaller droplets. Ice crystals are most often not spherical. Thus, the roles of shape, surface tension, gravity, and even surface chemistry on the dynamics have to be studied. These effects are also important in the thermodynamics of water droplet growth (discussed in section “[Thermodynamics of Phase-Change](#)”) and in the collisions-coalescence of water droplets (section “[Microphysics Without Thermodynamics](#)”).

Another important attribute is that over the length-scales that clouds occupy in the atmosphere, air is a compressible fluid. Note that the Earth’s atmosphere at a height of $10\ \text{km}$ is only a

Fluid Dynamics in

Clouds, Fig. 1 Cloud dynamics as the sum of its components



tenth as dense as it is on the ground. So a parcel of air, as it rises, will undergo significant expansion, which cannot be neglected by assuming incompressibility. The equations of compressible fluid motion are significantly more complicated than those of an incompressible fluid (which itself is a “Millennium problem”). The fully compressible equations of motion for air contain sound waves which operate on very short timescales. These sound waves are unimportant for the dynamics of interest to us and computing them would require short timesteps and greatly increase the computational requirements. Fortunately, since the Mach numbers Ma associated with the flow are small, the thermodynamic pressure of the ambient can be decoupled from the pressure fluctuations due to the motion (which are $O(Ma^2)$ relative to the thermodynamic means). This allows the use of the anelastic equations for flows over large heights or the incompressible equations for shallow flows, the latter of which is the limit we are concerned with. A sketch of the derivation of the anelastic and incompressible equations from the compressible equations may be found in Durran (1989) and Bannon (1996). As the name suggests, the anelastic equations “filter out” the sound waves from the dynamics, leaving only the effects of compressibility on the large scale dynamics. On relatively small scales, the assumption of incompressibility is reasonable and is typically made in studies of the flows in shallow clouds (Pauluis et al. 2010; Schumacher and Pauluis 2010; Weidauer et al. 2010; Pauluis and Schumacher 2011), and even in some

idealized studies of deep convection (Hernandez-Duenas et al. 2013).

As we see in Fig. 1, the dynamics of clouds is an interplay of particle inertia, thermodynamics, the resulting buoyancy-driven flow. At the largest scales, the effect of Earth’s rotation, and solar radiation and its modification by clouds, need to be understood better, and we do not deal with these topics in the present entry.

In summary, studies at different scales have to sometimes be carried out in isolation, using approaches and assumptions appropriate for that scale. New physics is revealed at each scale, and their effects must then be included in our studies at other scales.

Microphysics Without Thermodynamics

A simple framework, which ignores the effects of thermodynamics, phase changes, and the associated changes in temperature, to understand the physics of a *single* warm cloud is to model it as a dilute suspension of small, spherical water droplets of radius a which are advected by a statistically stationary, homogeneous, and isotropic, full-developed turbulent flow. Such an approach ignores the effect of condensation, arising from a super-saturated environment, by assuming that the starting point of such studies are non-precipitating droplets which are already condensed to sizes of about $10\text{ }\mu\text{m}$; hence further growth through condensation over a reasonably short time window, corresponding to the life-time

of such a cloud, is unlikely (Shaw 2003; Grabowski and Wang 2013; Lanotte et al. 2009; Bodenschatz et al. 2010; Devenish et al. 2012).

Such a simplification has at least two distinct advantages. Firstly, it allows us to formulate and address questions of collisions, coalescences, and gravitational settling (precipitation) in the turbulent setting of a cloud in a precise way. Secondly, given this framework, it lends itself easily to the use of tools and ideas developed in the field of turbulent transport over the last two decades or so.

In typical clouds, given $a/\eta \ll 1$, the Reynolds number associated with a droplet $Re_p \ll 1$. This allows us to define the dynamics of a droplet, in the presence of a gravitational force $\mathbf{g}$ and an (turbulent) advecting fluid velocity $\mathbf{u}$, in terms of its position $\mathbf{x}_p$ and velocity $\mathbf{v}$, through the linearized Stokes drag model with a Stokes time τ_p (Ravichandran et al. 2017a):

$$\frac{d\mathbf{x}_p}{dt} = \mathbf{v}; \quad (1a)$$

$$\frac{d\mathbf{v}}{dt} = -\frac{\mathbf{v} - \mathbf{u}(\mathbf{x}_p)}{\tau_p} + \mathbf{g}. \quad (1b)$$

The velocity field of the carrier flow, driven to a statistically steady state through a force $\mathbf{f}$, with density ρ_f , a kinematic viscosity ν , and a pressure field P , satisfies the incompressible, three-dimensional Navier-Stokes equation

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} = \nu \nabla^2 \mathbf{u} - \frac{\nabla P}{\rho_f} + \mathbf{f}; \quad (1c)$$

$$\nabla \cdot \mathbf{u} = 0. \quad (1d)$$

Given the assumptions of a small droplet and a dilute suspension, the underlying flow is assumed to be unaffected by the presence of such water droplets.

The effect of the finite size and the density contrast of the particle with the carrier flow, which leads to a finite time of relaxation of the particle velocities to that of the fluid, are captured by the Stokes time $\tau_p = \frac{2a^2 \rho_p}{9\nu \rho_f}$, where the particle density is given by ρ_p ; for clouds (water droplets

in air), the ratio of these two densities is $\rho_p/\rho_f \sim 1000$. However, it is useful to measure this inertia of the particles in terms of the non-dimensional Stokes number $St = \tau_p/\tau_\eta$, where $\tau_\eta = \sqrt{\nu/\epsilon}$ is the characteristic, short-time, Kolmogorov time-scale of the fluid (ϵ is mean energy dissipation rate). Such nondimensional numbers allow an easy comparison between observations, experiments, theory and numerical simulations.

The linear Stokes drag model (Eqs. 1a and 1b) is, of course, in the heavy-particle limit $\rho_p \gg \rho_f$, a simplification of the Maxey-Riley equation (Maxey and Riley 1983) for the motion of a spherical particle (with $Re_p \ll 1$) in a flow:

$$\begin{aligned} \rho_p \frac{d\mathbf{v}}{dt} = & \rho_f \frac{D\mathbf{u}}{Dt} + (\rho_p - \rho_f) \mathbf{g} \\ & - \frac{9\nu\rho_f}{2a^2} \left(\mathbf{v} - \mathbf{u} - \frac{a^2}{6} \nabla^2 \mathbf{u} \right) \\ & - \frac{\rho_f}{2} \left(\frac{d\mathbf{v}}{dt} - \frac{D}{Dt} \left[\mathbf{u} + \frac{a^2}{10} \nabla^2 \mathbf{u} \right] \right) \\ & - \frac{9\rho_f}{2a} \sqrt{\frac{\nu}{\pi}} \int_0^t \frac{1}{\sqrt{t-\xi}} \frac{d}{d\xi} \left(\mathbf{v} - \mathbf{u} - \frac{a^2}{6} \nabla^2 \mathbf{u} \right) d\xi \end{aligned} \quad (2)$$

where $\frac{D}{Dt}$ denotes the full convective derivative and it factors in the effects of the force due to the undisturbed flow $\rho_f \frac{D\mathbf{u}}{Dt}$, the buoyancy $(\rho_p - \rho_f)\mathbf{g}$, the Stokes drag $\frac{9\nu\rho_f}{2a^2} \left(\mathbf{v} - \mathbf{u} - \frac{a^2}{6} \nabla^2 \mathbf{u} \right)$, the added mass $\frac{\rho_f}{2} \left(\frac{d\mathbf{v}}{dt} - \frac{D}{Dt} \left[\mathbf{u} + \frac{a^2}{10} \nabla^2 \mathbf{u} \right] \right)$, and the Basset history $\frac{9\rho_f}{2a} \sqrt{\frac{\nu}{\pi}} \int_0^t \frac{1}{\sqrt{t-\xi}} \frac{d}{d\xi} \left(\mathbf{v} - \mathbf{u} - \frac{a^2}{6} \nabla^2 \mathbf{u} \right) d\xi$ effects. Without going into a rigorous demonstration of how Eq. 2 reduces to Eq. 1b, we can immediately see that for heavy particles the force due to the undisturbed flow is negligible and the only effect of gravity is a net acceleration downwards. Furthermore, the Faxen corrections $\sim a^2 \nabla^2 \mathbf{u}$ for small particles are negligible as is the Basset term in such dilute suspensions of passive particles. (On the last aspect, we refer the reader to a recent work by Prasath et al. (2019) for a detailed analysis of the Basset history term.) Indeed recent work by Saw et al. (2014) has confirmed by comparing experimental data with those obtained from a numerical simulation of Eqs. 1, that the approximations discussed here are indeed

reasonably valid for the dilute suspensions of small, but heavy, particles that we consider in this entry.

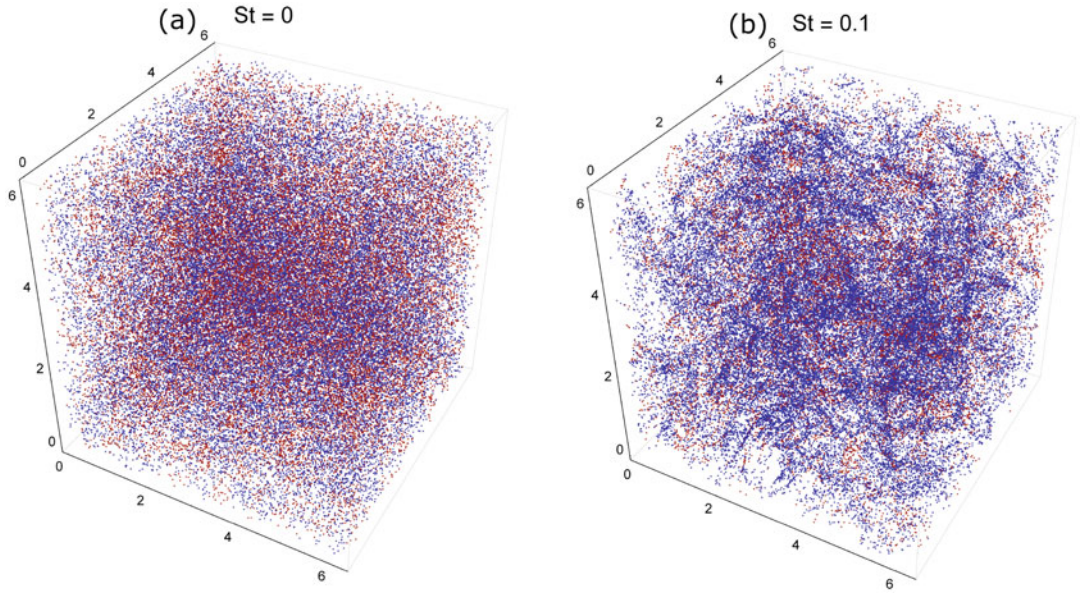
Before we proceed further, it might be useful at this stage to comment on how Eqs. 1 is solved on the computer (Canuto et al. 2006). (See Pandit et al. (2017) for a discussion on the nature of such simulations in two-dimensional flows.) The incompressible Navier-Stokes equations (Eqs. 1c and 1d) are typically solved, in three dimensions, on triply periodic cube of side 2π with N^3 collocation points; in the results being reviewed in this entry, N has ranged from 512 up to 2048 yielding Taylor-scale based Reynolds number which ranges from (approximately) 120 to 450. The flow is driven to a statistically steady, homogeneous, and isotropic, turbulent state with an external forcing. There is of course considerable freedom in the way we choose to force the fluid; two particularly popular choices are one with a constant energy injection at low wavenumbers (Sawford 1991) and another where (again at low-wavenumbers) a second-order Ornstein-Uhlenbeck process (Lamorgese et al. 2005) is adapted to provide a more *random* forcing. The equations themselves are solved through a standard pseudo-spectral method where spatial derivatives are taken in Fourier space to allow an easy integration in time of what essentially becomes an algebraic equation.

Solving for the particle dynamics (Eqs. 1a and 1b) is less involved. The only nontrivial element in this is to use suitable interpolation schemes to obtain the fluid velocity, which is calculated on a regular Eulerian grid, at typically off-grid particle positions. Several such schemes exist and the ones commonly used are the cubic spline, the B-spline, the trilinear, or the cubic interpolation schemes (see e.g. van Hinsberg et al. 2013).

The consequences of the linear Stokes drag model have been studied extensively (Bec et al. 2005; Chun et al. 2005; Bec et al. 2007; Monchaux et al. 2012; Gustavsson and Mehlig 2016; Ireland et al. 2016) since the pioneering work of Bec (Bec 2003; Bec 2005). A detailed discussion of this is certainly beyond the scope of this entry. However, in what follows, it is useful to recall two central features of the dynamics defined by Eqs. 1, namely *preferential concentration* and *caustics*.

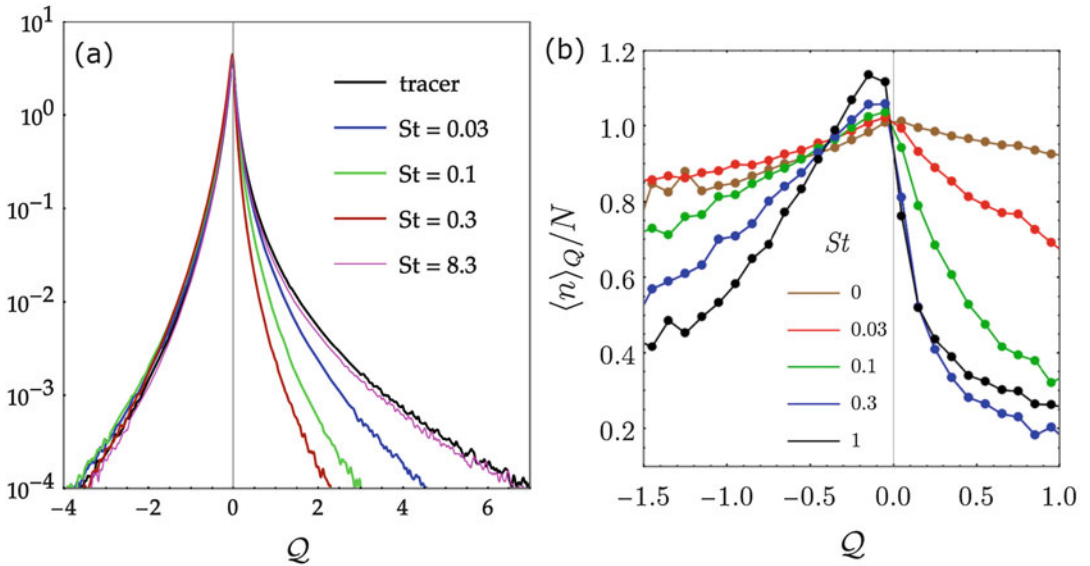
The dissipative dynamics of the particle motion leads to a preferential sampling of the flow and hence a preferential concentration of particles for finite Stokes numbers (seen in Fig. 2), as opposed to a homogeneous distribution in the flow seen for tracer particles with $St=0$. Particles with finite sizes evolve to (dynamically changing) attractors with fractal dimensions. Traditionally, this preferential concentration or inhomogeneities in the distribution of particles is captured through the correlation dimension D_2 obtained from calculating the probability $P^<(r)$ of two particles being within a distance r , with $P^<(r) \sim r^{D_2}$. The correlation dimension D_2 is of course a function of the Stokes number St . In the limit of vanishing St (tracers), particles must distribute homogeneously and hence, in a three-dimensional flow, $D_2 = 3$. For very large values of St , the motion of particles is essentially decorrelated from the flow and thus has a more ballistic behavior. This results, yet again, is space-filling and consequently $D_2 = 3$. At intermediate values of St , however, the particle distributions are inhomogeneous $D_2 < 3$ and maximal clustering (or inhomogeneities) is observed (with an accompanying minimum in D_2) for $St \sim O(1)$. We refer the reader to Figs. 1 and 2 in Bec et al. (2007) for an illustration of these effects.

From the perspective of flow structures, the clustering of heavy inertial particles can be tied to their ejection from vortical or rotational regions of the flow. One way to quantify this behavior is via the Q -criterion (Dubief and Delcayre 2000), which uses the local velocity gradient matrix $\mathcal{A}$ to define a quantity $Q \equiv (R_{ij}^2 - S_{ij}^2)/2$ (where $R = (\mathcal{A} + \mathcal{A}^T)/2$ and $S = (\mathcal{A} - \mathcal{A}^T)/2$). Regions dominated by rotation (straining) have $Q > 0$ (< 0). Figure 3a presents the Lagrangian probability distribution functions (PDFs) of Q measured along the trajectories of tracers and inertial particles with various values of St . The undersampling of vortical regions by inertial particles is clearly visible; indeed the effect is significant even for St as small as 0.03 (relevant for 10–20 μm cloud droplets). This effect gets stronger up to $St \approx 0.5$, beyond which the particles begin to decorrelate from the underlying flow structures, until eventually, for large St , the PDF approaches that for tracers (cf. $St = 8.3$ in Fig. 3a).



Fluid Dynamics in Clouds, Fig. 2 Snapshots of tracers (a) and inertial particles (b), with $St = 0.1$, in a three-dimensional turbulent flow. Particles in regions dominated by rotation ($Q > 0$) are colored red, while those in regions dominated by straining ($Q < 0$) are colored blue. The

dissipative dynamics of inertial particles ($St = 0.1$) causes them to form dynamic clusters, which are seen in panel (b) to mainly reside in straining regions, in accordance with the ejection of inertial particles from rotational zones



Fluid Dynamics in Clouds, Fig. 3 Panel (a) presents PDFs of Q sampled by tracers and inertial particles with various values of St . Panel (b) shows the average coarse-

grained particle number density, conditioned on the local value of Q , for various St

The fact that ejection from vortices leads to concentration and clustering in straining regions is apparent in Fig. 3b, which presents a coarse-

grained particle number density (using cubic bins of side 20η) conditioned on the local value of Q for various St . As St increases from zero, the

density of particles in regions of moderate straining increases, while the density in rotational regions reduces. This is illustrated visually by Fig. 2b, wherein most of the dense particle clusters are blue ($Q < 0$). Figure 3b also shows that particle density reduces with St in regions of very high straining, indicating that inertial particles cannot cluster in such intense regions of the flow, but rather prefer mildly straining zones.

A second important ingredient in this story is caustics (Ravichandran and Govindarajan 2015). Caustics are defined here as regions in the flow where droplets of different velocities can arrive simultaneously at the same location. In other words, caustics are regions of the flow where the droplet velocity cannot be described as a field. These are significant for the following reason. Droplets of moderate Stokes number (~ 0.1 to 1) get ejected quickly out of vortices, and this increases their propensity to collide and coalesce, but smaller droplets are usually taken to behave like passive scalars, just advecting passively with the flow. Under this assumption no preferential concentration takes place for small droplets, and collisions would be extremely rare. We thus do not have a mechanism by which small droplets can coalesce and begin to cross the bottleneck. In the immediate vicinity of a single vortex of circulation Γ , that is, within a distance $\sim \sqrt{\Gamma\tau_p}$ from the vortex centre, even the smallest droplets are centrifuged out (Ravichandran and Govindarajan 2015), and caustics can form. It was shown (Ravichandran and Govindarajan 2015; Deepu et al. 2017) that collisions between small droplets can be greatly enhanced in the caustics region, giving rise to a small number of droplets which can cross the bottleneck, and become the seeds for further coalescence events.

Given this context, let us return once more to questions within the framework of turbulent transport which are pertinent to the problem of droplet dynamics in a warm cloud. In particular, the questions that we discuss in this entry have to do with collisions, coalescences, and precipitation. Specifically these are best discussed by answering the following questions: How fast – and where – do droplets collide? How fast do droplets grow (by coalescence)? And, how fast do droplets settle

under gravity? (The issue of the structure of such aggregates when they collide, but not coalesce, will not be covered in this overview (Bec et al. 2013; Gupta et al. 2018).)

Turbulence is thought to play a dominant role in enhancing the droplet-droplet collision rates, and in turn the droplet-size distributions as well as the initiation time of rain, in typical warm clouds (Shaw 2003; Falkovich et al. 2002). The underlying mechanism instrumental in this is not only preferential concentration, discussed above, but also, through *slings* (Falkovich et al. 2002; Bewley et al. 2013) and *caustics* (Wilkinson et al. 2006; Falkovich and Pumir 2007), the extreme velocities with which particles can approach each other. Therefore in order to gain insights which can help build mesoscopic models for collision kernels, it is important to have reliable estimates of the typical relative velocities between droplets which are about to collide in a turbulent flow.

This issue was addressed by Saw et al. (2014) who, through experiments, numerical simulations, and theory, studied the probability distribution functions of the velocity differences between pairs of particles, measured along the line-of-sight, when they are quite close to each other. In the experiment, a turbulent flow was generated within a 1 m-diameter acrylic sphere (Bewley et al. 2013) with Taylor microscale Reynolds numbers R_λ as high as 190 corresponding to values of η as low as 180 μm . In such a flow, a bi-disperse population of droplets was introduced, via a spinning disc (Walton and Prewett 1949), with mean diameters 6.8 μm and 19 μm which are much smaller than η . Given that the experiment was able to achieve three different R_λ , and hence η , it was possible to obtain particle trajectories for six different Stokes numbers through stereoscopic Lagrangian Particle Tracking (Ouellette et al. 2006). Particle trajectories obtained from numerical simulations, with similar Stokes numbers and R_λ as the experiments, make meaningful comparisons of theory and experiment possible.

A convenient measure of the statistics of how droplets collide is through the probability distribution function of the longitudinal component of the velocity differences $v_{||}^i$ between pairs of

particles and conditioned on their separation r . In Fig. 1 of Saw et al. (2014), these distribution functions for four different values of the Stokes number and, in each case, conditioned on three different values of the separation r are shown. The agreement between the experimental and numerical data, especially for the larger values of St , is a confirmation of the validity of the linearized Stokes drag model of Eqs. 1. However, it is worth pointing out that these distributions, which seem to fit the form of stretched exponentials (Kailasnath et al. 1992) and at odds with the compressed exponential prediction for large Stokes numbers (Gustavsson et al. 2008), show consistently, for reasons still not clear, a greater convergence between the numerical and experimental data for the left tail (approaching pairs) than for the right tail (separating pairs). Furthermore, a closer examination of these distributions shows that droplet-pairs approach each other with increasing relative velocities – and a possible increase in collision rates – as their Stokes number increases consistent with other evidences of the sling effect (Bewley et al. 2013).

These distributions were of course conditioned on small ($O(\eta)$) but still finite separations; in the context of understanding collisions among droplets in a cloud, we should examine the relative velocities at contact or at least when they are even closer to each other ($r \rightarrow 0$). It turns out that all these distributions can be collapsed on top of one another (Fig. 2 in Saw et al. (2014)) by a simple rescaling with r^β ; experimental and numerical data suggests that β has a mild Stokes-dependence and for reasonably large values of St (not entirely valid for droplets in a cloud at its infancy), corresponding to extreme velocity differences, its value is consistent to the saturation exponent ξ_∞ of the higher-order moments of relative velocities (Bec et al. 2010). The positive exponent β , which is small for small droplets, nevertheless suggests the possibility of mild impact velocities on contact.

The particle dynamics in a more realistic cloud is of course nonstationary as droplets grow and change their sizes and numbers. A step in this direction is to account for the polydispersity in a suspension. James and Ray (2017) investigated

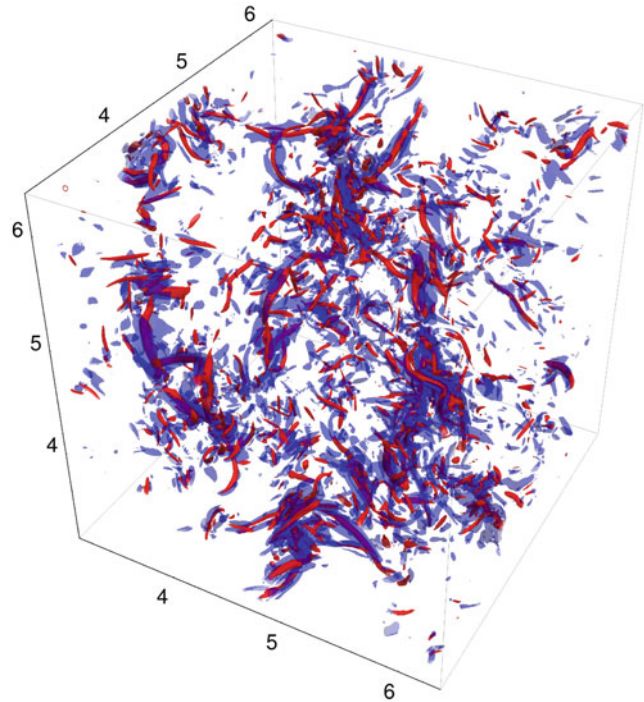
this problem for suspensions in two- and three-dimensional turbulent flows. Interestingly, the authors were able to derive the typical impact velocities between particle pairs which, in principle, could have different Stokes numbers. This was conveniently done by assuming a reference particle with a Stokes number St_1 and a second one with St_2 ; in the usual mono-disperse problem, $St_2 = St_1$. Assuming the smoothness of the underlying fluid velocity at small interparticle separations, the impact velocity Δ was theoretically calculated (under suitable approximations) for pairs of droplets with different Stokes numbers and validated against numerical simulations.

As we discussed before, because of the collision-coalescence processes, it is safe to assume that particle dynamics in a cloud may well be nonstationary. As a result of this James and Ray have also looked at the collision rates in a nonstationary phase and found an enhancement of this, when compared to the collision rates in the statistically stationary phase for all nonzero Stokes numbers. Interestingly, this ratio peaks to 2 (Fig. 4 in James and Ray (2017)) when the Stokes number of the colliding pairs is around 0.2. Although the results obtained suggest a lack of universality, this observation might be one possible explanation of possible run-away processes which explains the rapid growth of droplets from tiny nuclei, seed rain drops. We also refer the reader to recent studies in Gustavsson and Mehlig (2011, 2013), Meibohm et al. (2017), Bhatnagar et al. (2018a, b) on the issue of such polydisperse suspensions and the relative velocities of colliding inertial particles in turbulent flows.

All of this inevitably leads us to the question of how the size distribution of droplets evolves when we turn on actual coalescences in a suspension advected by a turbulent flow. A time-honored theoretical framework for studying such problems is the Smolochowski's equation with a stationary coalescence rate or kernel. Starting with an initial infinite bath of particles of the same size (and mass), such an approach inevitably leads to a growth in the population of droplets of larger sizes as a simple power-law in time. Specifically, assuming an initial infinite bath of particles of mass 1, the number of particles with mass i

Fluid Dynamics in

Clouds, Fig. 4 Snapshot of intense rotational (red) and straining (blue) regions in a turbulent flow, visualized using the Q -criterion. Intense vortical/rotational regions take the form of tubes or *worms* that are enveloped by strongly straining sheet-like structures, forming vortex-strain wormrolls. (Reproduced from Picardo et al. 2019)



(also, in these units, an integer since coalescence imposes mass conservation) grows as

$$n_i(t) \sim e; n_1^i(t/t_i)^{i-1}. \quad (3)$$

(The time t_i appearing in the exponent is taken as an average time-scale set by the different stationary collision rates between all particle pairs which add up to give the i -th particle.)

However, when such particles are in a dilute suspension carried by a turbulent flow, how accurate are these estimates emerging from Smulochowski's equation? This question was answered, through a combination of theory and numerical simulations, by Bec et al. (2016). This work carefully analyzed the contribution to the coalescence rate coming not from the microphysics of adhesion but the fact that particles are in a turbulent flow. This nontrivial contribution was shown to factor in the anomalous part δ_3 in the scaling of the third-order structure function in a turbulence-advected passive-scalar field $\langle (\theta(\mathbf{x} + \mathbf{r}) - \theta(\mathbf{x}))^3 \rangle \sim |\mathbf{r}|^{1-\delta_3}$ and leads to a population growth of the form

$$n_i(t) \sim e; n_1^i(t/t_i)^{(1-\frac{3}{2}\delta_3)(i-2)+1}. \quad (4)$$

Given that the (universal) value of $\delta_3 \approx 0.18$, this form suggests a more rapid growth of droplets with masses different from the bath of monomers of mass 1.

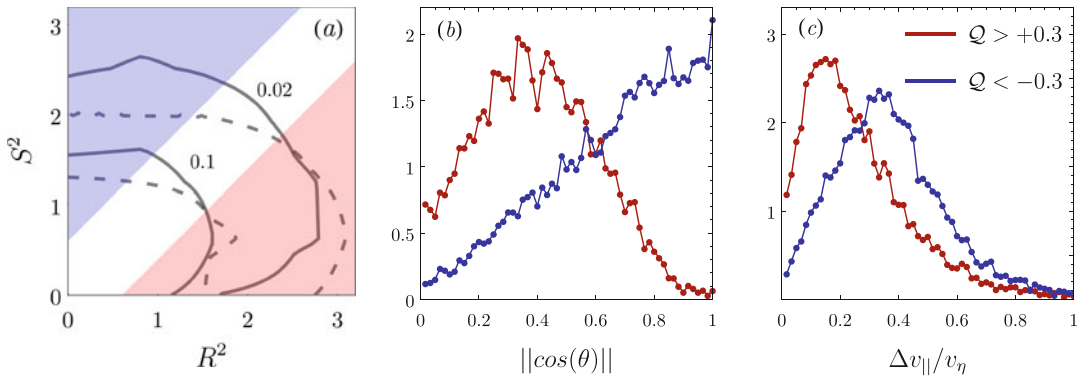
The accuracy and correctness of the theoretical calculations were benchmarked against the state-of-the-art direct numerical simulations with an initial suspension of one billion monomers which were then allowed to coalesce and form droplets of other sizes in the same paper (Bec et al. 2016). Figure 2 in this work shows the accuracy of the prediction (4) at early times; a further confirmation of the importance of anomalous scaling was obtained via the probability density function of the inter-coalescence times between the initial monomers (of mass 1) and other droplets of different sizes which were subsequently formed (Fig. 3 in Bec et al. (2016)). Remarkably, these results are perhaps the only ones that show how anomalous scaling in turbulence shows up as a leading order effect in a more applied problem such as the one of coalescences in turbulent transport.

This work thus established a plausible argument to suggest a rapid growth in droplets at short times through a complex (Lagrangian) correlated sequence of events. However, the fate of these droplets at long time still remains a large unexplored issue.

All of these measurements are of course central in building up models for collision and coalescences in a warm cloud. However, they do not help us, in a direct way, to uncover the correlation, if any, between collisions and the flow structures peculiar to turbulence. Indeed, even small-scale, homogeneous and isotropic turbulence, which we may expect to encounter in the core of a cumulus cloud, is rich in structure: It is perforated by a hierarchy of rotational and straining flow structures (She et al. 1990; Douady et al. 1991; Jiménez and Wray 1998; Zeff et al. 2003; Schumacher et al. 2010; Davidson et al. 2012), as shown in Fig. 4. These structures are a physical manifestation of the intermittency of the velocity gradient field, which distinguishes fully-developed turbulence from a simple random Gaussian field (Ishihara et al. 2007; Pandit et al. 2009; Tsinober 2009). One may ask, therefore, whether the collisions between inertial particles or droplets are sensitive to these flow structures, and thereby to the non-Gaussian nature of

turbulence. This question was addressed recently by Picardo et al. (2019), who measured the relative values of rotation (R^2) and straining (S^2) at the locations of collisions, and compared them to the values sampled by particle trajectories. They found that collisions among small St particles are disproportionately frequent in straining regions, much more than what may be anticipated from preferential concentration alone. In fact, this effect is not fundamentally tied to inertia, but persists even in the limit of $St \rightarrow 0$, for which the particles are homogeneously distributed. (In this limit, the particles are effectively tracers, but with a small fictional radius that enables the detection of collisions.)

Figure 5a presents contours of the joint probability distribution of the values of R^2 and S^2 , measured both where inertia-less particles reside (dashed contours) and where they collide (solid contours). Here, straining (rotational) regions with $Q < -0.3$ ($> +0.3$) are shaded in blue (red). Clearly, there is an oversampling (undersampling) of straining (vortical) regions by collisions, compared with the particle trajectories. This discrepancy is a result of the very different flow geometry in these regions. Colliding particles in straining regions tend to approach each other in a head-on or rear-end fashion,



Fluid Dynamics in Clouds, Fig. 5 Panel (a) presents the 0.1 and 0.03 level contours of the joint probability distribution function of the values of R^2 and S^2 , measured at the positions of inertia-less ($St = 0$) particles (dashed) and at their collision locations (solid). Panels (b) and (c) present distributions of the collision angles and the collision velocities, respectively, conditioned on whether the collisions occur in rotational ($Q > +0.3$, red) or straining ($Q < -0.3$,

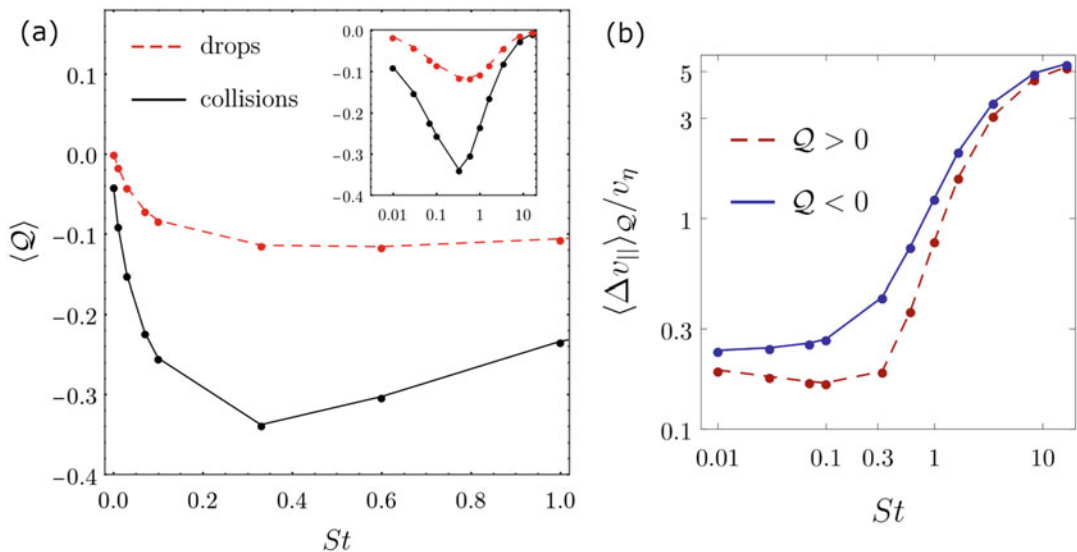
blue) regions. The contribution of these regions to the joint distribution in panel (a) is shown by the red/blue shading. Taken together, these panels show that collisions in straining regions tend to occur in a head-on or rear-end fashion, which results in a higher collision approach velocity, and thereby a higher collision frequency. (Reproduced from Picardo et al. 2019)

whereas particles in rotational regions approach each other in a side-on manner and undergo glancing collisions. This is shown by the conditioned-PDFs of the collision angle θ (the angle between the relative velocity and position vectors of the two colliding particles), presented in Fig. 5b. For a given magnitude of the underlying fluid velocity, head-on collisions are faster than side-on collisions, as shown in Fig. 5c, because a larger component of the relative-velocity of the particles is translated into the collision velocity. For the same number density of particles, this results in a higher collision frequency in straining regions.

Particle inertia acts to enhance this preference of collisions for straining regions, up to $St \approx 0.3$. This is seen in Fig. 6a, which presents the average value of $Q = (R^2 - S^2)/2$ measured at particle and collision locations, as a function of St . At small St , inertia selective enhances the collision velocity in straining regions, as shown in Fig. 6b, and therefore increases the frequency of collisions in straining regions relative to rotational regions. At larger values of St , however, the particles begin to decorrelate from the underlying flow structures and both particle and collision locations begin to

distribute uniformly (cf. the inset of Fig. 6a) and also collide with comparable velocities in straining and vortical regions (Fig. 6c). This mismatch between where inertial (for small St) particles reside and collide was earlier observed by Perrin and Jonker (2014), who also analyzed the influence of flow structures on collisions using the eigenvalues of the velocity gradient matrix (Perrin and Jonker 2016), which enable a finer classification of structures than the simple Q -criterion.

We have seen that collisions between small St particles are sensitive to the local underlying structure of the flow. As St approaches unity, however, collisions are affected not just by the structure at the collision location, but by all the flow structures encountered by the particles, up to a time of about τ_p prior to the collision, or up to a distance of $|\mathbf{v}|\tau_p$ around the collision. This raises the possibility of intense vortical and straining regions conspiring to generate violent, rapid collisions, due to their peculiar vortex-strain worm-roll geometry (cf. Figure 4): Particles in intense vortex tubes will be ejected with large slip velocities into the enveloping straining sheets, where they have a high chance of colliding with large



Fluid Dynamics in Clouds, Fig. 6 Panel (a) presents the average value of Q measured where inertial particles or droplets collide (black-solid) and reside (dashed-red), as a function of St . The inset presents the same result for a wider range of St using a semi-log scale. Panel (b) presents the

average collision velocity, conditioned on whether collisions occur in regions dominated by rotation (red) or strain (blue), as a function of St . (Adapted from Picardo et al. 2019)

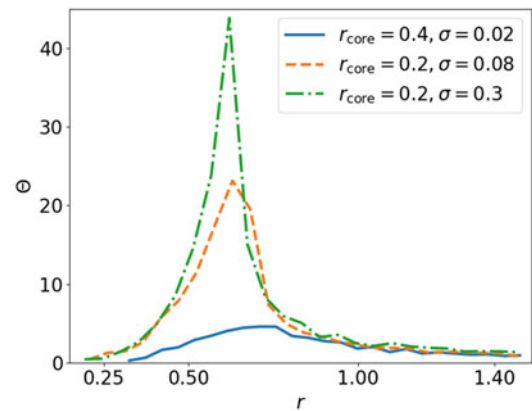
relative velocities. Picardo et al. (2019) found evidence for this scenario, by Lagrangian backtracking of particles that collided in straining regions: the particles that collided in the least time after being ejected from a vortex were indeed the ones that originated from the strongest vortices, collided in the strongest straining regions and with the largest collision velocities.

This effect of vortex-strain worm rolls was found to be prominent only for St beyond about 0.5. This value may seem too large for small cloud droplets, and indeed it is when one considers the particle relaxation time relative to the mean Kolmogorov time-scale of the turbulent flow. However, at the extremely large Re of in-cloud turbulence, there are likely to be a few, very intense, intermittent vortices, with a local flow time scale that is much smaller than the mean Kolmogorov time-scale. This means that local, *effective* St of particles in the vicinity of such intense vortices will be closer to unity, making the vortex ejection and collision scenario relevant. Even if such intense vortices occupy a very small volume fraction of the flow, the rapid collisions generated will be able to act as a seed that initiates the runaway growth of droplets by gravitational driven collision-coalescence (Kostinski and Shaw 2005).

Unfortunately, the Re values that can be directly simulated on a computer are still orders of magnitude smaller than what is expected for a cloud. Therefore, it is not possible to directly investigate the effect of high- Re flow structures. However, one can gain a basic understanding of how such structures may influence the motion and collisions of droplets by using model vortex flows. Such an analysis was carried out in two dimensions, using point and Gaussian vortices, by Ravichandran and Govindarajan (2015) and Deepu et al. (2017), and later extended to a three-dimensional Burgers vortex (1948) by Agasthya et al. (2019). These studies show that particles near the core of a strong vortex are ejected more rapidly than particles farther away. This leads to a large increase in the local particle density around the periphery of the vortex (Fig. 3 of Agasthya et al. (2019)), as well as large relative velocities between neighboring particles (caustics). These factors combine to significantly

enhance collisions in the vicinity of the vortex. Figure 7 shows the coarse-grained collision density Θ (obtained from a large ensemble of simulations) as a function of the radial distance r from the axis of a Burgers vortex, which serves as a model for the intense vortex tubes (Gibbon et al. 1999; Davidson 2004) observed in three-dimensional turbulence (cf. Fig. 4) (She et al. 1990; Douady et al. 1991). Three cases are presented, corresponding to a mild, wide vortex ($r_{\text{core}} = 0.4$) and an intense thin vortex ($r_{\text{core}} = 0.2$), with mild and strong axial straining ($\sigma = 0.08$ and 0.3, respectively). The straining flow along the vortex axis is seen to enhance the number of collision produced around an intense vortex, by drawing particles in toward the core of the vortex.

Taken together, these results show that collisions are definitely sensitive to the structure of the turbulent flow, and suggest that the intense and intermittent vortex-strain structures, characteristic of turbulence, may play a key role in the coalescence driven growth of droplets in clouds.



Fluid Dynamics in Clouds, Fig. 7 Coarse-grained collision density Θ , that is, the number of collision per unit volume, as a function of the radial distance r from the axis of a tubular Burgers vortex. r_{core} is a measure of the size of the core of the vortex, that is, of how intensely the vorticity is concentrated about the vortex-axis. σ is a measure of the straining flow that is directed inward along the radial direction and outward along the vortex-axis. This straining is essential for maintaining a concentrated vortex tube in a viscous fluid, where vorticity continuously diffuses outward (Davidson 2004). Here, we see that this straining flow also acts to enhance the collisions around intense vortices. (Reproduced from Agasthya et al. 2019)

Before we conclude this section, let us touch upon briefly the question of how such droplets settle under gravity. The mean settling velocity V_s , that is, the component of the particle velocity along the direction of gravity, of a particle with a Stokes time τ_p is simply (1b) $V_s = \tau_p g - \langle u_z(\mathbf{x}_p, t) \rangle$. In the absence of a flow or a uniform sampling of the flow by the particles, $\langle u_z(\mathbf{x}_p, t) \rangle = 0$ and leading to a predictable settling velocity $V_s = \tau_p g$. However, in the presence of a background turbulent flow, it has been known that the settling velocity can be enhanced through an oversampling of the regions where the fluid velocity is downwards. A systematic and quantitative understanding of this phenomenon was carried out by using extensive numerical simulations and theory by Bec et al. (2014).

A convenient way to estimate this enhancement of the settling velocity is to measure the relative increase $\Delta_V = (V_s - \tau_p g)/(\tau_p g) = -\langle u_z(\mathbf{x}_p, t) \rangle/(\tau_p g)$ as a function of the Stokes number. In Fig. 2 of Bec et al. (2014), the authors showed the Δ_V is indeed positive and a non-monotonic function of St with a peak at $St \sim 1$. This enhancement, in the limit of small values of St , was understood by showing that the correlation $\langle u_z \nabla_\perp \cdot \mathbf{v} \rangle = \tau_p^2 g \langle (\partial_z u_z)^2 \rangle > 0$. This shows that clustering of particles on any horizontal plane (perpendicular to the direction of gravity) – and hence $\nabla_\perp \cdot \mathbf{v} < 0$ – occurs at points in the flow where the fluid velocity is downwards since for the overall correlation function to be positive $u_z < 0$. Such an asymptotics also suggests that for small Stokes numbers $\Delta_V \propto St$.

The large Stokes asymptotics, dominated by the ballistic motion of particles resulting in a short-time correlation with the fluid velocity being sampled by the particle, is more involved. However, the remarkable thing about this asymptotics is it makes a scaling prediction on Δ_V in terms of the Reynolds, Froude, and Stokes numbers which are shown, through numerical simulations (Fig. 2 in Bec et al. (2014), to be exceptionally accurate.

From the perspective of warm clouds, the nature of setting of droplets under gravity has one further important consequence. Bec et al. (2014) showed that gravitational settling, especially when the

effect of gravity is pronounced, is accompanied by a quasi-two-dimensionalization of the particle dynamics (Fig. 3 in Bec et al. (2014)). A consequence of this is the estimation of the collision rate $\kappa \sim r^\gamma$ which is the average longitudinal velocity differences between pairs of same-sized particles at a separation $r \sim 2a \ll \eta$ as they approach each other. It was shown that since $\gamma = \xi_1 + D_2 - 1$, where ξ_1 is exponent of the order-1 structure function constructed from particle velocities, the approach rates must be influenced by the nature of clustering D_2 brought about through gravitational settling. Figure 4 in Bec et al. (2014) summarizes these exponents with their dependence on both the Stokes and Froude numbers and shows how, under the influence of gravity, interparticle approach velocities are diminished, through a renormalized effective Stokes number, as the effect of gravity begins to dominate. Indeed, these results suggest that for 30 μm -sized water droplets, typical in warm clouds, collision rates are almost doubled when we factor in the interplay of both gravitational and turbulent effects on their mixing. These ideas of settling are now being extended to spheroidal particles in turbulent flows which serve as an effective model for ice crystals in colder clouds (Roy et al. 2018; Anand et al. 2019).

The findings above are obtained at moderate Reynolds number, while the Reynolds numbers in a cloud are several orders of magnitude higher. We highlight the importance of understanding how flow structures and other features change with increasing Reynolds numbers. Moreover buoyancy effects can be important, as discussed below.

Microphysics with Thermodynamics

In the previous section we discussed how turbulence affects the dynamics of droplets, clustering droplets into high-strain regions, and enhancing droplet collision-coalescence. We assumed that droplets do not affect the turbulence. Mechanically speaking, this is a fair assumption through most stages of droplet growth. This is because water droplets are very small, and form a very dilute suspension, in that occupy only a millionth of the volume in a cloud. However, droplets can distort

the turbulence that drives them through the thermodynamics associated with phase change. Some of the physics behind these effects was explained in Ravichandran and Govindarajan (2017).

Thermodynamics of Phase-Change

The condensation of water vapor into water and the evaporation of liquid water into vapor (hereafter just phase-change) are governed by the Clausius-Clapeyron law,

$$\frac{dp_s}{dT} = \frac{L_v p_s}{R_v T^2}, \quad (5)$$

where p_s is the equilibrium water vapor pressure at the temperature T , L_v is the enthalpy of vaporization, and R_v is the gas constant for water vapor. The Clausius-Clapeyron law can be derived from the condition that the vapor-liquid system is at equilibrium at the given temperature (see, e.g., Bohren and Albrecht 1998, Chap. 5). This equation can be integrated assuming L_v and R_v are constants (this is a reasonable assumption) to give

$$p_s = p_s^0 \exp \left(\frac{L_v}{R_v} \left[\frac{1}{T_0} - \frac{1}{T} \right] \right). \quad (6)$$

Further approximation is possible for small temperature changes ($T_0 \approx T$) to give

$$p_s = p_s^0 \exp \left(\frac{L_v (T - T_0)}{R_v T_0^2} \right). \quad (7)$$

Due to its exponential nature, the amount of water vapor that can exist in equilibrium is a rapidly changing function of the ambient temperature; the equilibrium vapor pressure roughly doubles for every 10 K increase in temperature.

While the Clausius-Clapeyron law governs the *equilibrium* vapor pressure, it says nothing about *how* this equilibrium is to be reached. Chemical reactions or changes of phase that are thermodynamically favored may nevertheless not occur because the reactions have high energies of activation. As a result, pockets of air with higher concentrations of water vapor than given by Eq. 6 are very commonly found in the atmosphere. The system of air and water vapor is then

said to be “supersaturated.” In fact a cloud is often on average supersaturated. So excess water vapor is available, which can then condense. However, spontaneous condensation requires supersaturations of about 400%, while supersaturation values in the atmosphere are rarely greater than 5%. We therefore need cloud condensation nuclei on which condensation can occur, and droplets and aerosol particles provide such surfaces. These nuclei are typically small particles of salt or dust and a background concentration of these nuclei of about 100–1000 cc^{-1} exists in the atmosphere. This number concentration is a function of how polluted the air is, typically being larger over the continents than over the ocean. This number concentration, then, also decides how supersaturated the air can be. Supersaturations for polluted air are typically 1% or lower, while higher supersaturations are seen in marine clouds (see, e.g., Pruppacher and Klett 2010, Chap. 2). Nuclei smaller than a critical size (called the Kohler radius) reach an equilibrium radius and do not grow beyond this (due to the fact that the saturation vapor pressure is a function of the radius). Nuclei that are larger than the Kohler radius grow to become water droplets in clouds. These water droplets continue to grow by absorbing the water vapor in the atmosphere. The resulting release of the latent heat of vaporization drives the large-scale dynamics of clouds, as we sketch below.

A relation describing the rate at which the water droplets grow and consume water vapor can be derived assuming the water droplets are small enough for ventilation effects to be negligible (see Bohren and Albrecht 1998, Chap. 7; Pruppacher and Klett 2010, Chap. 13). This gives

$$a \frac{da}{dt} = \frac{s - 1}{C \rho_w},$$

where $C = O(10^7)$ ms/kg is a thermodynamic constant which is a function of the ambient temperature. The rate of growth of a droplet is inversely proportional to its radius. As we have seen in section “[Microphysics Without Thermodynamics](#),” this is one of the factors that makes explaining rain-formation challenging. If this relation is applied to a system of n droplets per unit

volume, ignoring interactions, the rate at which the water vapor in the system is consumed is

$$\frac{1}{\rho_s^0} \frac{d\rho_v}{dt} = -\frac{\rho_v/\rho_s - 1}{\tau_s}, \quad (8)$$

where τ_s is a time-scale, $\rho_s = p_s/(R_v T)$ is the saturation vapor density, and ρ_s^0 is a base value $\rho_s(p_0, T_0)$. This condensation of vapor results in the heating of the flow at a rate

$$\frac{dT}{dt} = \frac{L_v \rho_s^0}{C_p} \left(\frac{\rho_v/\rho_s - 1}{\tau_s} \right).$$

The latent heat of vaporization, $L_v \approx 2.5 \times 10^6$ J/kg/K, is a large value. As a result of this, despite the small amounts by weight of water vapor and liquid found in clouds (typical values are $O(1-10)$ g/kg), the amounts of heat released are enormous and can be $O(\text{MW/m}^3)$ (see, e.g., the discussion in Narasimha et al. (2011) on typical heating rates in clouds). The heating thus provided increases the temperature, and the resulting buoyancy drives the upward flow of the cloud. Differential heating of regions of the flow and the resulting buoyancy differences drive the turbulence in the flow. We look next at how particle inertia, phase change, and buoyancy interact in clouds.

Interactions of Particle Inertia, Thermodynamics, and Buoyancy-Driven Flow

We refer again to the box-diagram in Fig. 1 showing the different interacting phenomena in clouds. All clouds are composed of water vapor, water droplets, and aerosol particles suspended in turbulent flow. Particle inertia, phase-change, and buoyancy-driven turbulent flow are all active in clouds. However, depending on the type of cloud and the range of parameters, simplifying approximations may be made which ignore one or more of these effects. We discuss some relevant examples below which illustrate this.

Cumulus Clouds: Phase-Change+Buoyancy+Turbulence

Cumulus clouds are tall, heap-like clouds found in the atmosphere, and are crucial to the maintenance of heat and mass balance in the atmosphere. Their

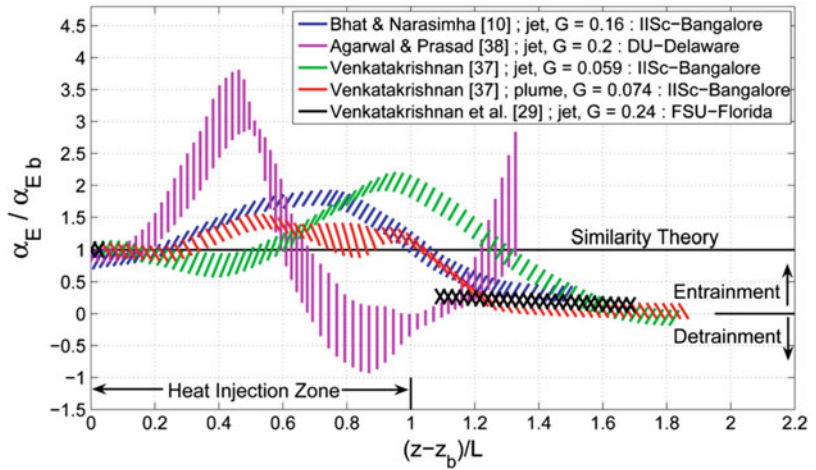
importance in the dynamics of the atmosphere has long been recognized, with competing attempts to model them as various free-shear flows like jets, plumes, or thermals (Stommel 1947; Squires and Turner 1962). These clouds, driven by the release of latent heat in the flow, differ significantly in their dynamics from jets and plumes without such latent heating, and have been an object of study for 60 years. A fuller review of these efforts may be found in De Rooy et al. (2013). The parameter of interest in the study of these clouds is the entrainment rate – the rate at which the cloud drags in ambient (dry) air from its environment. Entrainment dilutes the cloud, leading to its ultimate demise. Entrainment in free-shear flows is still a topic of active research, and the addition of volumetric (i.e., not at the source on the ground) heating complicates the picture.

Progress has been made through laboratory experiments on cumulus clouds, showing the role of the latent heat release (Narasimha et al. 2011), building on work in Bhat and Narasimha (1996), Venkatakrishnan et al. (1998, 1999). The addition of latent heat to the flow seems to not only accelerate the flow but to shut down the entrainment of ambient air into the bulk of the flow. This shut-down of entrainment (shown in Fig. 8) is argued to be because the heating disrupts the coherent structures in the shear layer of the flow (Narasimha et al. 2011; Bhat and Narasimha 1996). This then leads to the cloud remaining undiluted for longer and reaching higher altitudes than if the flow were a pure plume or jet.

As we have mentioned, the heating in the cloud arises out of the condensation of water vapor onto liquid water droplets in the cloud, and thus a full description of the dynamics would include all the phenomena listed in Fig. 1. However, especially for growing cumulus clouds which have not reached the precipitating state, the droplet size may be assumed to be small enough that the particle inertia is negligible. This is a reasonable assumption since the size distribution in non-precipitating cumulus clouds peaks at $10 \mu\text{m}$. This being the case, the droplet inertia is small and the droplets follow the velocity of the fluid. This in turn allows the droplets to be coarse-grained into a liquid-water field, a step that saves significant computational effort. Despite the

Fluid Dynamics in Clouds, Fig. 8

The entrainment coefficient in heated plumes first increases and then decreases to zero (i.e., the plume stops entraining). (Reproduced from Narasimha et al. 2011)



challenges involved, progress has been made because of the simplifying assumptions discussed. Large eddy simulations of cumulus clouds showing this behavior have been reported by Romps and Kuang (2010). Laboratory experiments of cumulus clouds have been reported by Narasimha et al. (2011). Direct numerical simulations for achievable Reynolds numbers are reported in Ravichandran and Narasimha (2020).

Mammatus Clouds: Phase-Change + Particle Settling + Buoyancy

A type of cloud that is perhaps not as consequential as the cumulus clouds, but no less fascinating, is the mammatus cloud. Typically found underneath cumulonimbus anvil outflows, and therefore acting as harbingers of inclement weather. The reasons for the formation of these clouds is a matter of ongoing research, and a comprehensive review of the various proposed mechanisms may be found in Schultz et al. (2006), with follow-up studies in Kanak and Straka (2006), Kanak et al. (2008). A promising explanation involves the combination of the settling of water droplets out of the cumulonimbus anvils, their subsequent evaporation forming a layer of air below the anvil that is denser than the ambient air, and the eventual instability due to this density inversion. Unlike in section “Cumulus Clouds: Phase-Change+Buoyancy+Turbulence,” particle settling cannot be neglected. Ravichandran et al. (2020) find that the size of the mammatus lobes is proportional to the settling velocity (which increases

for small droplet sizes like the square of the droplet size) and to the time-scale for phase-change (which is proportional to the inverse of the mean droplet size and the number concentration).

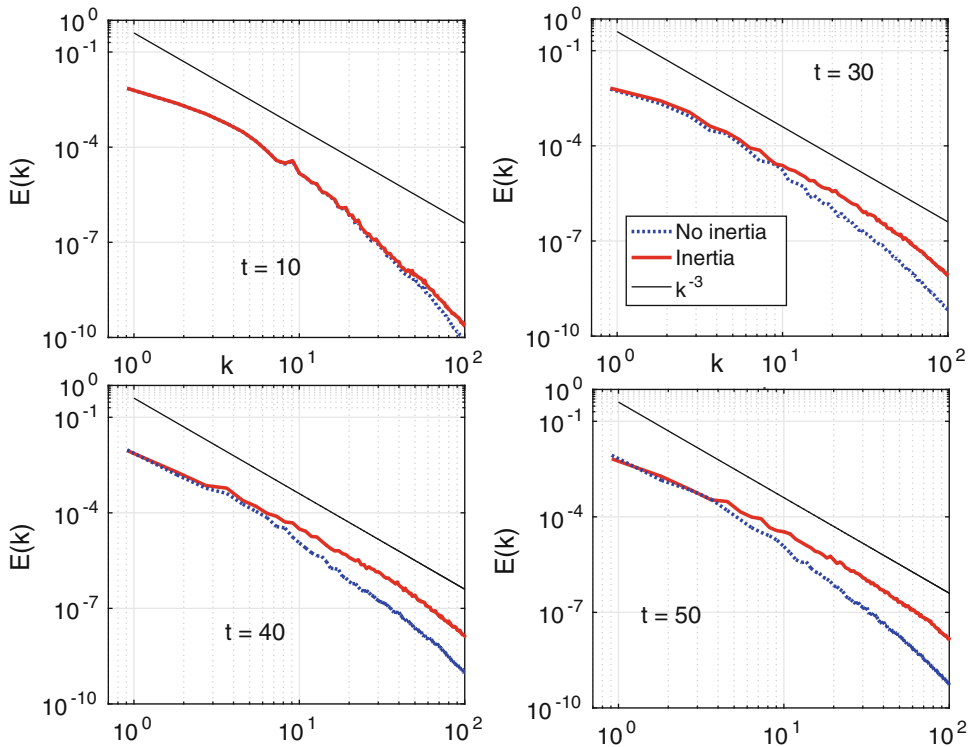
Droplets in Clouds, Redux: Particle Inertia+Turbulence+Phase-Change

The phenomenon of warm-rain initiation and the droplet-growth bottleneck that has been a long-standing unsolved problem in cloud physics, as discussed in section “Microphysics Without Thermodynamics.” In studies focusing on the fluid mechanics of droplet collisions-coalescence, the effects of phase-change and thermodynamics are typically neglected. In the regime of interest – when droplets have grown to large enough sizes that their growth rates are small – this assumption is justifiable. For most of the lifetime of a cloud droplet, however, the thermodynamics of condensation cannot be neglected. The interactions of phase-change and particle inertia are thus relevant in the dynamics of clouds: broad droplet size distributions are important in the rapid growth of falling droplets through coalescence with smaller droplets.

A first step in understanding the interactions of particle inertia and thermodynamics was taken by Shaw et al. (1998) who study how droplets interact with vortices. Clouds, being turbulent flows, are a tangle of strong vortices. Vortices, then, are suitable models for idealized studies. As we have seen in section “Microphysics Without Thermodynamics,” vortices expel inertial particles. When these inertial

particles are also nuclei for condensation, the cores of vortices are voided of nuclei for condensation and therefore have higher vapor concentrations than the outside. Shaw et al. (1998) argue that this should have two consequences: first, that any droplets that remain trapped in the vortical region will end up experiencing larger-than-average supersaturations, and thus be able to grow to sizes not predicted by only considering cloud-average values of supersaturation; second, that the supersaturations produced in the cores of the vortices should lead to the nucleation of condensation nuclei well above cloud-base, which allows a broadening of the droplet size distributions (on the lower side). The use by Shaw et al. (1998) of this mechanism in explaining warm-rain initiation has been questioned in the literature (see, e.g., Grabowski and Vaillancourt (1999) and Vaillancourt et al. (2001, 2002)), but the central message that particle inertia and thermodynamics interact in complex ways remains relevant, in our view.

Clouds are, as we have seen, turbulent flows where the turbulence is driven by the energy provided by condensing water vapor. While large velocities can be generated by large values of buoyancy, turbulence itself, as we have also argued, is generated by *spatial inhomogeneities* in the heating. Ravichandran and Govindarajan (2017) propose a model of how this can be achieved starting from initially homogeneous conditions, thereby providing a route by which turbulence can sustain itself by “feeding” on the latent heat of vaporization. The mechanism builds on the aforementioned effect of inertial particles being centrifuged out of vortical regions. This leaves the vortices more supersaturated (as in Shaw et al. (1998), but keeping track of temperature changes), but also colder than their surroundings which have been heated by the condensation of water vapor. The resulting density inhomogeneities lead to baroclinic torques which generate vorticity and thus turbulence in the flow (Fig. 9). We mention in passing that the buoyant



Fluid Dynamics in Clouds, Fig. 9 The energy density $E(k)$ versus the wavenumber k in simulations with and without accounting for the effects of particle inertia. The addition of particle inertia effects provides a route for the

transfer of energy to smaller scales starting from homogeneous conditions. Similar to a figure in Ravichandran and Govindarajan (2017)

vortices that result have interesting dynamics of their own (see Ravichandran et al. 2017b).

Growing clouds are also a class of free-shear flows. The edges of clouds, where the shear layers separate saturated regions from unsaturated regions, are thus regions of large inhomogeneities in vapor and droplet concentration. This results in the generation of strong sustained turbulent flow. Kumar et al. (2012, 2013, 2014) study this dynamics in an idealized setup where the temperature is held constant, but water droplets are allowed to grow or shrink in response to local conditions. The authors argue that, as a consequence of the high flow Reynolds numbers in a cloud, the mixing of dry ambient air with the saturated cloudy air will be highly inhomogeneous: that is, that parcels of saturated air and parcels of subsaturated air will often be found close to each other. As a result, particles in the shear layer can have complicated growth histories; the size distribution of such droplets will also be very broad as a result. They quantify this inhomogeneity in terms of a Damkohler number which is a ratio of the time-scale of phase-change to a characteristic timescale of the flow. In the high Reynolds number flows in the shear layers of clouds, they show that using a large Damkohler number $Da \gg 1$ results in highly skewed tails with a large number of droplets that begin at the edge of the shear layer experiencing extreme evaporation and thus shrinking significantly, while droplets in the saturated core of the flow grow slightly. In the later stages of a cloud's evolution, as large droplets formed in the cloud settle out of the cloud, they are likely to encounter these smaller droplets. The efficiency of collisions is significantly greater if the droplet sizes are different, and the presence of much smaller droplets in the shear-layers could play a crucial role in rain formation.

More recently, the entire process of rain formation from monodisperse cloud droplets has been studied by Gotoh et al. (2016) and Saito and Gotoh (2018). The authors develop a moving box model where they account for the upward velocity of a cloud by changing the mean background properties seen by the box. This allows them to follow a subvolume of the cloud as it ascends upwards. The cloud droplets initially grow by condensation of vapor. These cloud droplets eventually lead to a small number of larger droplets by collisions with

each other. This is a weak effect, since collisions of similarly sized particles are rare. The larger droplets that eventually form start to settle at significant velocities, and grow rapidly because of collisions-coalescence with the smaller droplets. The authors report that the intensity of the turbulence which is artificially chosen plays a key role in the collisions-coalescence process, in line with expectations from work on the problem over the last two decades.

Conclusion and Future Directions

The fluid dynamics of clouds is only part – if the most complex part – of climate science. We have argued here that understanding the dynamics is important in the face of the uncertainties of climate change. We hope to have convinced readers of the immense challenges and opportunities the field presents, both as an exercise in scientific curiosity and because of the far-reaching implications. Both these facets arise from the range of length- and time-scales present in the dynamics. The approach we favor – of understanding the parts in service of understanding the whole – has led to several semi-independent programs of research which have to be eventually be unified. Under present computational limitations the goal of these studies is to be able to parameterize the dynamics and improve global climate models.

Some areas of active research where the questions are reasonably well-defined and can be addressed computationally are (a) a fuller understanding of entrainment in free-shear flows in general, and cloud-flows in particular. Open problems include the magnitude of the entrainment and the details of the process by which volumetric heating alters the entrainment; by extension, entrainment in merging plumes/cumulus clouds as a way of understanding the dynamics of convective aggregation; and the incorporation of the resultant better models for entrainment into global climate simulations: perhaps by extending the super-parameterization method (see Randall et al. 2003). (b) Droplet-resolved simulations for collision-coalescence, in order to overcome limitations of the geometric collisions approach; to include effects of droplet splintering, droplet interactions, and flow-droplet coupling; and to include

effects of differences in liquid/gas properties like density, temperature, conductivity in the phase-change process.

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Collective Transport and Depinning

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Article Outline

Glossary

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Glossary

Elastic manifold An elastic manifold is a spatially extended object whose energy is given by a quadratic function of the gradients of its transverse displacements. In statistical physics, it is used as a coarse-grained description of the low-energy modes in an ordered structure.

Pinning Pinning is a common phenomenon in condensed systems where the relevant degrees of freedom are trapped to an energy minimum and hence respond dynamically only when the external driving exceeds a certain threshold. Pinning is often caused by defects or impurities in the system but it may also be due to intrinsic properties such as the existence of a periodic lattice that breaks the translational symmetry of space.

Scaling Scaling describes power-law relationships among two or more physical quantities. Physical systems at continuous phase transitions are often found to exhibit scale invariance, i.e., structural and dynamic properties on different length and time scales can be mapped onto each other through suitable scale transformations. Such properties are characterized by a set of scaling exponents. The renormalization group theory, through its flow equations under a scale transformation, provides a systematic method to compute these exponents.

Universality Universality is a key concept in the classification of systems which exhibit scale invariance. Models in the same universality class have identical scaling properties and are described by the same set of scaling exponents. Therefore the identification of possible universality classes is one of the key issues in the study of, e.g., critical phenomenon at continuous phase transitions. The origin of universality is best illustrated by the fixed-point structure of the renormalization group flow equations. Studies have shown that dimensionality, symmetry, and conservation laws are the key factors that determine a particular universality class. There is, however, a great deal of theoretical interest to identify new principles that determine universality classes, or exceptions to the above rule, particularly in driven nonequilibrium systems.

Definition of the Subject

Collective transport takes place in systems which exhibit highly correlated response to external driving. This is in contrast to, e.g., electrical conduction in a normal metal, where free electrons drift independently under an applied electric field, leading to Ohm's law. Collective motion of microscopic degrees of freedom, on the other hand, often yields a nonlinear response or even threshold behavior, where steady-state transport sets in only when the driving exceeds a certain critical

strength. In the subcritical regime, the collective modes are pinned by defects or impurities in the system. An increasing degree of correlation and corporation takes place as the threshold is approached. The subject plays an important role in the study of a broad class of solid state phenomena, including charge and spin density wave transport, hysteresis in dirty magnets, and non-linear current-voltage characteristics in type-II superconductors. It has also found interesting applications outside physics, such as in crack propagation and earthquake modeling. Important theoretical developments that took place in the early 1990s culminated in the formulation of a functional renormalization group theory for the no equilibrium deepening transition. The analytical framework enables systematic computation of the critical properties and, perhaps more importantly, elucidation of universality through its fixed point structures. Subsequent work by many research groups have established a close link between driven deepening and the sand pile models of self-organized criticality (SOC). This connection has been fruitfully explored to gain a better understanding of the long-range spatial correlations and intermittent temporal activities in the two classes of problems.

Introduction

The motion of a water drop down a glass window under gravity illustrates many salient features of collective transport and deepening, although the phenomenon itself is surprisingly rich in physics and chemistry when examined in microscopic detail (de Gennes 1985; Leger and Joanny 1992; Podgorski et al. 2001). The size of the drop is governed by the so called capillary length (typically of the order of a few millimeters) from elementary physics: On this scale the surface tension that makes a water drop spherical competes with the gravity which acts to deform the droplet. The actual descent of the droplet, which usually follows a zigzag path with an ever changing speed, is a result of many factors, not least the random force set by the local wettability of the glass surface. With a microscope, one may

observe the hysteric advancement of the contact line separating wet and dry regions on the substrate. The interplay between the surface tension, the pinning force on the contact line, and the driving force provided by gravity gives rise to a complex and intermittent dynamical behavior encompassing a wide range of length and time scales.

Similar types of collective and intermittent transport exist in solids. In certain low-dimensional materials such as NbSe₃, periodic modulation of the electronic density, known as the charge-density-wave (CDW) (Grüner 1988), develops spontaneously at sufficiently low temperatures through the Peierls instability. An applied electric field in the direction of the charge modulation exerts a body force on the CDW much the same way as gravity does on the water droplet. However, in the presence of impurity atoms or crystal defects, the CDW does not move unless the electric field exceeds a certain threshold value, as seen in experiments (Grüner 1988; Thorne 2005). The vortex lattice in type-II superconductors is another example of modulated electronic structures within a solid (Larkin 1970). Pinning of the vortex lattice by intrinsic or artificial defects is essential for achieving a high critical supercurrent in these materials.

Yet another class of collective pinning phenomena in solids involves the dynamics of topological defects such as crystal dislocations (Granato and Lüke 1956) or magnetic domain walls (Bruinsma and Aeppli 1984). These objects have internal dimensions lower than that of the embedding medium, and hence can explore inhomogeneities in the surrounding environment. The driven motion of these objects has a great effect on the physical properties of their host system, e.g. plastic deformation of a solid due to glide and climb motion of dislocations, and hysteresis effect (Ryu et al. 2007; Sethna et al. 1993; Zapperi et al. 1998) related to the pinning of domain walls separating regions of opposite magnetization.

The development of quantitative theories for impurity pinning and the driven depinning transition began in the 1970s after fundamental breakthroughs in many-body physics and equilibrium critical phenomena (Fukuyama and Lee 1978;

Larkin 1970; Larkin and Ovchinnikov 1979; Lee and Rice 1979). Research in this area has traditionally followed two separate approaches: The microscopic approach that attempts to explain the observed behavior starting from the fundamental laws of physics, and the phenomenological approach that focuses on the large-scale properties using the simplest models possible. The second approach, which is popular in the field of statistical physics, has the advantage of mathematical simplicity and clarity. It facilitates identification of the underlying symmetries of the original problem, and the establishment of universality classes through which model systems can be classified and compared. However, real physical systems often contain complications that prevent a direct comparison between model predictions and experimental observations (see, e.g. Thorne 2005). This is where the microscopic approach, popular among condensed matter theorists, comes to aid. In the best studied cases, a microscopic theory allows one to derive or estimate system-specific parameters and properties, and to suggest correct phenomenological models and possible improvements when discrepancies are found.

The present article focuses on the recent theoretical developments in the statistical physics of this class of problems. This is partly motivated by the significant progress that has been achieved in a quantitative characterization of the depinning transition over the past two decades. Similar to the critical phenomena in thermal equilibrium systems, static and dynamic fluctuations exhibit scaling properties with exponents that fall into well-defined universality classes determined by the symmetry and dimensionality of the problem. These concepts allow one to establish precise relationships among models proposed under different physical contexts. The successful application of the renormalization group methods to the depinning transition has led to a deeper analytical understanding of the observed critical phenomena. Our choice is also motivated by the close connection between depinning and the subject of self-organized criticality (Bak et al. 1987), which enjoys broad interest in the complexity community.

We shall start with a brief review of systems, mostly from solid state physics, where collective

modes and depinning play an important role in the interpretation of the observed transport phenomenon. A generic mathematical formulation of this class of problems, known as the elastic manifold in a disordered potential, is introduced, along with a discussion of the complex energy landscape underlying its equilibrium and dynamic properties. This is followed by a description of the critical properties at the driven depinning transition and numerical results. The basic analytic structure of the threshold solution can be seen in a mean-field theory. We then summarize the main results of functional renormalization group calculations which provide a systematic and quantitative characterization of the depinning transition. The relationship between driven depinning and self-organized criticality is explained. The influence of medium anisotropy on the depinning transition is briefly discussed. Finally, we mention a few open problems in the field for future work.

Elastic Manifolds and Impurity Pinning

Elasticity, Order, and Symmetry Breaking

Although long-range spatial correlations that underlie collective transport can be generated dynamically under certain conditions, we shall focus on systems for which such correlations are already present before external driving is applied. In particular, we shall assume that the system is in a low temperature ordered state and responds elastically to external perturbations. This assumption allows us to concentrate on the large scale properties of the system in the depinning process, while leaving the microscopic, system-specific behavior to a separate discussion.

Elasticity is a familiar concept in macroscopic physics. An object is said to be *elastic* if it deforms under an applied force in a continuous and reversible manner. Microscopically, elasticity is intimately related to the existence of an ordered state that breaks a continuous symmetry (Anderson 1984). This point can be appreciated with the example of a crystalline solid. Atoms in the solid form a periodic structure in space with energetically preferred unit cells and lattice constants. This state is said to break the translational

symmetry of the particle system as the density of atoms is no longer uniform in space. A uniform translation of the structure does not lead to a change in the system energy. On the other hand, relative displacement of atoms distorts the unit cells and leads to an increase in energy which grows quadratically with the displacement. Thus, the system has acquired a form of rigidity by breaking a continuous symmetry to gain order. Elasticity is a manifestation of this rigidity when the ordered state is perturbed by external forces or internal impurities and defects.

Both charge-density waves and vortex lattices are periodic structures in space, and hence naturally their behavior is similar to a crystalline solid. There are, however, differences in the number of components needed to describe a generic deformation in each case. A CDW with a single modulation wave vector $\mathbf{Q}$ corresponds to an electron density $\rho(\mathbf{r}) = \rho_0 + \rho_1 \cos(\mathbf{Q} \cdot \mathbf{r} + \varphi)$, where ρ_0 is the average density and ρ_1 the modulation amplitude due to charge ordering. A uniform phase shift $\varphi \rightarrow \varphi + c$ moves the CDW uniformly against the underlying lattice. Weak deformation of the CDW is described by a spatially varying phase $\varphi(\mathbf{r})$. The elastic energy of a CDW depends quadratically on the phase gradient $\nabla\varphi$, with different elastic constants along and perpendicular to the modulation vector $\mathbf{Q}$ (Fukuyama and Lee 1978). In the case of the vortex lattice, a two-component vector field $\mathbf{u}(\mathbf{r})$ perpendicular to the vortex lines is needed to describe a general distortion of the ideal structure. The construction of the elastic energy parallels that of a crystalline solid. In an isotropic medium, three elastic constants are needed to describe the energetics of a vortex line array (Larkin 1970; Larkin and Ovchinnikov 1979).

Topological defects in an ordered structure also behave elastically when deformed from their ideal positions under a great variety of circumstances, though this form of elasticity has a different microscopic origin. A dislocation in a solid, for example, has a core where the atomic arrangement differs from elsewhere in the crystal. This gives rise to an excess amount of energy proportional to the length of the line. The interface between two bulk phases has an excess free energy (commonly known as the surface tension) proportional to the

surface area for the same reason. This applies also to domain walls in a magnet.

Elastic Manifolds in a Disordered Potential

The energy of a topological defect is affected by the presence of impurities or point defects in the system. For example, an impurity atom sitting in the core of a dislocation has a different atomic environment and hence a different energy than when it resides in a normal region. This effect gives rise to a short-range and often attractive force between the impurity and the dislocation core. The tendency for the dislocation to distort itself in order to adapt to the impurity configuration is countered by the elastic energy cost. In general, the two competing forces lead to a large number of metastable conformations of the dislocation core, separated by energy barriers. The effect of impurities on interfaces and magnetic domain walls can be considered in a similar way.

A unified statistical mechanical description of impurity pinning can be formulated in terms of a D -dimensional elastic manifold embedded in d spatial dimensions (Fisher 1986; Halpin-Healy and Zhang 1995; Le Doussal et al. 2004). Let $\mathbf{r} \in R^D$ be the internal coordinates of the manifold and $\mathbf{u}(\mathbf{r}) \in R^{d-D}$ be the transverse displacement of the manifold at point $\mathbf{r}$ with respect to a flat configuration. When the deformation is small, the excess volume of the manifold is a quadratic function of the gradient of $\mathbf{u}(\mathbf{r})$. The following energy function includes effects of both elasticity and impurities,

$$E(\{\mathbf{u}\}) = \int d^D r \left[\frac{\gamma}{2} |\nabla \mathbf{u}|^2 + V_R(\mathbf{r}, \mathbf{u}) \right]. \quad (1)$$

Here γ is the stiffness constant of the manifold, and $V_R(\mathbf{r}, \mathbf{u})$ is a random potential arising from the interaction between the manifold and the impurities in the medium. In most theoretical treatments, the set of random variables $\{V_R(\mathbf{r}, \mathbf{u})\}$, which take particular values in a given sample, is assumed to be Gaussian distributed with the mean $\langle V_R(\mathbf{r}, \mathbf{u}) \rangle = 0$ and the second moment $\langle V_R(\mathbf{r}_1, \mathbf{u}_1) V_R(\mathbf{r}_2, \mathbf{u}_2) \rangle = R(\mathbf{u}_1 - \mathbf{u}_2) \delta(\mathbf{r}_1 - \mathbf{r}_2)$. Here $\delta(\mathbf{r})$ is a short-ranged function which vanishes beyond a coarse-graining length $a_{\parallel}$.

The form of the disorder correlator $R(\mathbf{u})$ in the transverse directions is dictated by the symmetries of the original physical problem (Fisher 1986). For contact interactions and randomly distributed impurities in the embedding space, $R(\mathbf{u})$ is short-ranged with a characteristic decay length $a_\perp$. A different situation is encountered when the manifold represents an interface that separates two bulk phases, each affected differently by the impurities which serve as a “random field” (i.e., the impurity atom has different chemical potential in the two bulk phases). The potential $V_R(\mathbf{r}, u)$ represents the cumulative effect of impurities swept by the interface when it is displaced to $u(\mathbf{r})$ from a reference configuration. Consequently $R(u) \sim |u|$ for large u .

A CDW in the presence of impurities can also be described by Eq. (1), where $u(\mathbf{r}) = \varphi(\mathbf{r})$ is a scalar field and $d = D$. Since the impurity interacts with the local charge density which is a periodic function of the local phase, the potential $V_R(\mathbf{r}, \varphi)$ is also periodic in φ . Consequently, $R(\varphi)$ is periodic in φ as well.

Application of Eq. (1) to the vortex lattice requires special care. On scales smaller than the spacing between vortex lines, each vortex line behaves as an independent object. However, this description fails on large scales, where the periodicity of the lattice changes the nature of the problem (Giamarchi and Le Doussal 1994; Nattermann 1990).

Rugged Energy Landscape, Critical Dimension, and the Pinning Length

The two terms in Eq. (1) represent competing effects on the manifold: Elasticity favors a flat manifold with a constant $\mathbf{u}$, while the attractive force from impurities gives rise to a spatially varying $\mathbf{u}(\mathbf{r})$. The configuration $\mathbf{u}(\mathbf{r})$ which minimizes Eq. (1) satisfies the following force-equilibrium condition:

$$\gamma \nabla^2 \mathbf{u} - \nabla \mathbf{u} V_R(\mathbf{r}, \mathbf{u}) = 0. \quad (2)$$

Complications arise when Eq. (2) has many solutions. Each solution corresponds to a local minimum of the energy function (1), separated by energy barriers from other local energy

minima. The resulting energy surface (or landscape) is known as *rugged*.

Proper characterization of the energy landscape defined by Eq. (1) has been a long-standing problem in the statistical mechanics of disordered systems. For $D < 4$ and weak disorder, the ruggedness appears when the system size is greater than a characteristic length L_c along the manifold, known as the *pinning length*. This important observation was due to Larkin (1970) for flux lines, Fukuyama, Lee and Rice (Fukuyama and Lee 1978; Lee and Rice 1979) for CDWs, and Imry and Ma (1975) for magnetic domain walls. On scales $L < L_c$, elasticity limits the transverse displacement $\mathbf{u}$ (known as roughness) to be within the respective correlation length $a_\perp$ of the impurity potential $V_R(\mathbf{r}, \mathbf{u})$, so that the manifold lies within a single minimum of the energy surface. On the scale L_c , the typical strength of the random force $\nabla_{\mathbf{u}} V_R$, averaged over a volume L_c^D , is estimated to be $|\overline{\nabla_{\mathbf{u}} V_R}| \simeq \frac{R^{1/2}(0)}{a_\perp} L_c^{-D/2}$. Balancing it with the elastic force $\gamma a_\perp / L_c^2$, one obtains,

$$L_c = \left(\frac{\gamma^2 a_\perp^4}{R(0)} \right)^{1/(4-D)}. \quad (3)$$

For $L > L_c$, Eq. (2) has an exponentially increasing number of solutions.

For $D > 4$, the elastic term in (2) dominates over the random force term on large length scales. Consequently, the rugged energy landscape is a small scale phenomenon which occurs when L_c is larger than the correlation length $a_\parallel$ of the disorder potential $V_R(\mathbf{r}, \mathbf{u})$ parallel to the manifold. From Eq. (3) we see that this condition requires the disorder strength to be sufficiently strong. Weak disorder is not able to produce pinning for manifolds with internal dimension greater than 4.

The qualitative analysis above shows that the energetics of the manifold problem are qualitatively different below and above four dimensions. The existence of a *critical dimension* $D_c = 4$ suggests systematic renormalization group approach to the problem. However, earlier attempts based on a perturbative treatment of the disorder potential failed to produce a renormalizable theory (Aharony et al. 1976; Efetov and Larkin 1977; Grinstein 1976). This was first achieved successfully by Daniel

Fisher (1986) in 1986 in the equilibrium case. Extension of the scheme to the driven depinning transition is discussed in section “Analytical Treatments of the Depinning Transition and Universality”.

Driven Depinning, Critical Properties, and Scaling

The Driven Depinning Transition

An applied force $\mathbf{F}$ coupled linearly to the displacement field $\mathbf{u}(\mathbf{r})$ tilts the equilibrium energy landscape as defined by Eq. (1) towards a particular direction. For small $\mathbf{F}$, the manifold makes small adjustments locally to reach a new stationary state where force equilibrium is re-established, and this happens for the majority of solutions to Eq. (2). The number of such solutions, however, continues to decrease as $\mathbf{F}$ increases. When the magnitude of $\mathbf{F}$ exceeds a certain critical value, all stationary states disappear, and the manifold enters a running state. The transition from stationary to running states with increasing $\mathbf{F}$ is known as the *driven depinning transition*.

Figure 1 illustrates the dependence of the steady-state velocity v of the manifold against $F = |\mathbf{F}|$. In the absence of thermal fluctuations, there is a well-defined threshold F_c that separates the pinned from moving regimes. At finite temperatures, the transition from a pinned to a moving manifold is smeared out by thermally activated creep motion. At low temperatures, the rounding effect is weak except in a very small region around F_c .

The discussion in subsection “Rugged Energy Landscape, Critical Dimension, and the Pinning Length” on the pinning length can be used to

estimate the critical force needed to depin the manifold. For $D < 4$, the maximum pinning effect is seen on the scale L_c , where the typical strength of the first two terms in (5) is given by (Bruinsma and Aeppli 1984; Feigel'man 1983; Lee and Rice 1979).

$$F_c \simeq \gamma a_{\perp} / L_c^2 = \frac{R^{2/(4-D)}(0)}{\gamma^{D/(4-D)} a_{\perp}^{(4+D)/(4-D)}}. \quad (4)$$

This is also the force needed to depin the manifold. For $D > 4$, pinning is possible only if $L_c > a_{\parallel}$ or $R^{1/2}(0) a_{\perp}^{-1} a_{\parallel}^{-D/4} > \gamma a_{\perp} / a_{\parallel}^2$, i.e., the strength of the pinning force is stronger than that of the elastic force on the minimal scale $a_{\parallel}$.

Continuum Model of the Manifold Dynamics

A dynamical model for the manifold can be constructed by assuming the motion to be completely overdamped. This is quite reasonable for the applications mentioned in section “Introduction”, where the displacement $\mathbf{u}(\mathbf{r}, t)$ represents a course-grained variable which changes on a time scale much longer than the relaxation time of underlying microscopic processes. With this assumption, the equation of motion for the manifold takes the form,

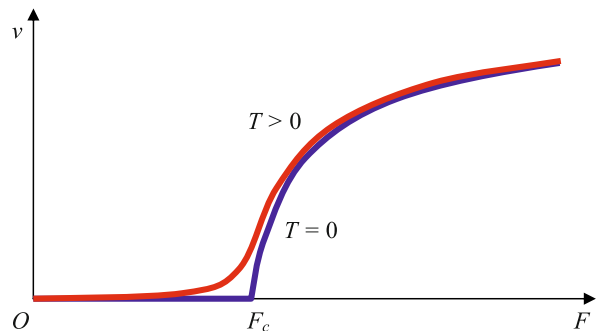
$$\mu^{-1} \frac{\partial \mathbf{u}}{\partial t} = \gamma \nabla^2 \mathbf{u} + \eta(\mathbf{r}, \mathbf{u}) + \mathbf{F}.$$

Here μ is known as the mobility of the manifold, and $\eta(\mathbf{r}, \mathbf{u}) = -\nabla_{\mathbf{u}} V_R(\mathbf{r}, \mathbf{u})$ is the random pinning force.

An interface is described by a height function $u(\mathbf{r}, t)$, so that the dynamical equation, which

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Fig. 1 Schematic plot showing the manifold velocity v against the driving force F at zero (blue) and finite (red) temperatures. Below the threshold F_c , the manifold is pinned by impurities in the medium, but thermal activation may generate a small but finite velocity



defines the so-called *linear interface model* (LIM), takes a scalar form (Bruinsma and Aeppli 1984; Feigel'man 1983),

$$\mu^{-1} \frac{\partial u}{\partial t} = \gamma \nabla^2 u + \eta(\mathbf{r}, u) + F. \quad (5)$$

The same equation applies to a CDW, but with $\eta(\mathbf{r}, u + 2\pi) = \eta(\mathbf{r}, u)$ periodic in the phase variable (Fisher 1985). Using the example of a single vortex line in three dimensions, Ertas and Kardar (1994a) have shown that the extra transverse dimensions do not change the main features of the depinning process. Hence Eq. (5) can be considered as the generic description of the driven manifold problem, where $u(\mathbf{r}, t)$ stands for the component of the transverse displacement in the driven direction.

In Layman's terms, Eq. (5) may be viewed as describing the advance of a military front where the attacking side has more ammunition and manpower F but the defending side is able to exploit the hilly ground positions $\eta(\mathbf{r}, u)$ to pose an effective resistance. In addition, stretching the front line into a convoluted form results in a decrease in attacking power and is hence discouraged!

For the analysis of Eq. (5), it is convenient to describe pinning effects in terms of the random force $\eta(\mathbf{r}, u)$ instead of the random potential $V_R(\mathbf{r}, u)$. Without loss of generality, one may assume the mean value of $\eta(\mathbf{r}, u)$ to be zero. For Gaussian distributed random forces, it is suffice to specify the statistics of $\eta(\mathbf{r}, u)$ with the correlator,

$$\langle \eta(\mathbf{r}_1, u_1) \eta(\mathbf{r}_2, u_2) \rangle = \Delta(u_1 - u_2) \delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (6)$$

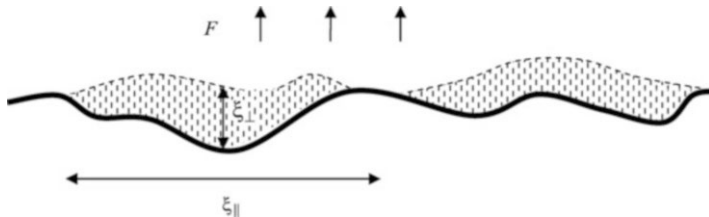
On the “bare” scale, $\Delta(u) = -\partial^2 R / \partial u^2$ but as shown in (Le Doussal et al. 2002; Narayan and Fisher 1993), this relation breaks down in the driven case upon coarse-graining of the original degrees of freedom.

Critical Properties and Scaling Laws

Let us first consider the interface depinning problem as described by Eq. (5). This model has been studied extensively both analytically (Chauve et al. 2001; Narayan and Fisher 1993; Nattermann et al. 1992) and numerically (Leschhorn 1993; Rosso et al. 2003) in recent years, and the main characteristics of the solution have been well-understood. These findings are summarized below.

The form of Eq. (5) suggests a “non-crossing condition” as first noted by Middleton (Middleton 1992a). Consider two interface configurations $u_1(\mathbf{r}, t_0)$ and $u_2(\mathbf{r}, t_0)$ at some initial time t_0 . If $u_1(\mathbf{r}, t_0) < u_2(\mathbf{r}, t_0)$ for all $\mathbf{r}$ on the interface, one can easily show that $u_1(\mathbf{r}, t) < u_2(\mathbf{r}, t)$ at any later time $t > t_0$, i.e., the two solutions never touch if initially one is completely behind the other. This property in particular implies that the interface velocity $v = \overline{du/dt}$ (averaged over all sites $\mathbf{r}$) in the steady state is a unique and continuous function of F , ruling out first order phase transition in this class of models.

On the moving side but close to the depinning threshold, advancement of the interface can be described with the help of Fig. 2. The thick line illustrates the interface position at a given time t_0 . Pinning yields a roughness which grows as a power-law of the distance between two points on the interface, i.e.,



Collective Transport and Depinning, Fig. 2 An interface above but close to the depinning threshold. Depinning events within a correlation length $\xi_{\parallel}$ and correlation time τ

are highly correlated and obey scaling at the transition. Shaded area represents the volume swept by the interface over the time interval τ

$$\langle [u(\mathbf{r}, t_0) - u(\mathbf{r}', t_0)]^2 \rangle \sim |\mathbf{r} - \mathbf{r}'|^{2\zeta}, \quad (7)$$

where ζ is known as the *roughness exponent*. This behavior holds on a range of length scales from the pinning length L_c to a correlation length $\xi_{\parallel}$ along the interface. The transverse displacement of the interface on scale $\xi_{\parallel}$ is given by $\xi_{\perp} \sim \xi_{\parallel}^{\zeta}$.

Motion of the interface within a correlation time τ also obeys scaling. On time scales shorter than τ , the interface advances through a sequence of rapid, localized movements (known as avalanches) of varying size up to the scale $\xi_{\parallel}$. The average time for a given site to move by a distance Δu grows as a power law: $\Delta t \sim \Delta u^{1/\beta}$. During this time, activities within a distance $l \sim \Delta t^{1/z}$ along the interface are correlated. The exponent $z = \zeta/\beta$ is known as the *dynamical exponent*. This scaling terminates when l reaches the correlation length $\xi_{\parallel}$, or $\Delta t = \tau \sim \xi_{\parallel}^{z/\beta}$, where the interface as a whole advances to a new disorder environment with a different distribution of pinning sites and pinning forces.

As F decreases towards F_c , the size of each correlated domain grows to infinity in a power-law fashion as well, e.g., $\xi_{\parallel} \sim |F - F_c|^{-\nu}$, where ν is known as the *correlation length exponent*. The three exponents ζ , z and ν together characterize the critical properties of the interface at the depinning transition. Through dimensional arguments, one may determine the critical behavior of quantities other than those discussed above. For example, the interface velocity near the transition can be estimated from $v \simeq \xi_{\perp}/\tau \sim \xi_{\parallel}^{\zeta}/\xi_{\parallel}^{z/\beta} \sim |F - F_c|^{\nu(z-\zeta)}$, hence the corresponding *velocity exponent* is given by,

$$\theta = \nu(z - \zeta) \quad (8)$$

The region between two interface configurations separated by time τ , as shown in Fig. 2, can be described as a set of “bubbles”, each representing a correlated volume of base area $\xi_{\parallel}^D$ and height $\xi_{\perp}$. The average strength of the pinning forces within each bubble has a variation of the order $\xi_{\parallel}^{-D/2} \xi_{\perp}^{-1/2}$ from the system-wide average. Variation of this quantity among bubbles should

be smaller than the excess driving force $F - F_c$ so that depinning can take place uniformly across the system. This condition is fulfilled if the correlation length exponent satisfies the following inequality (Harris 1974; Narayan and Fisher 1993; Nattermann et al. 1992).

$$\nu \geq \frac{2}{D + \zeta} \quad (9)$$

The above description of interface depinning applies also to the CDW with one important caveat. Due to the non-crossing condition, steady-state motion of the CDW at $F > F_c$ is periodic in time, i.e., $\varphi(\mathbf{r}, t + \tau) = \varphi(\mathbf{r}, t) + 2\pi$ for all $\mathbf{r}$, with τ being the period of the attractor (Middleton 1992a). The dynamic phase advance at different sites has thus bounded variations described by $\zeta = 0$. Above but close to F_c , the activity at a given site, as measured by the phase velocity $\dot{\varphi}(\mathbf{r}, t)$, is typically concentrated in time windows much shorter than T , but acquires long-ranged spatial correlations up to a correlation length $\xi_{\parallel} \sim (F - F_c)^{-\nu}$. Both analytical (Narayan and Fisher 1992) and numerical calculations (Myers and Sethna 1993) indicate that $\nu = 1/2$ in all dimensions, therefore violating Eq. (9). Although the origin of this behavior has not been settled completely (Narayan and Middleton 1994), a plausible explanation is that fluctuations of the pinning force in a given region of the system are compensated by a static phase distortion $\varphi_0(\mathbf{r}) = \varphi(\mathbf{r}, t = 0)$, so that the system behaves much more homogeneous than the naïve estimate used to obtain Eq. (9). The sample-to-sample fluctuations of F_c , on the other hand, have been shown recently (Bolech and Rosso 2004; Fedorenko et al. 2006) to obey a Gaussian distribution with a width proportional to $L^{-D/2}$ as predicted, where L stands for the linear system size.

Numerical Results for the Critical Exponents

The depinning transition of the elastic manifolds and the CDW has been studied extensively using various lattice models. Middleton and Fisher (1991, 1993), Myers and Sethna (1993), and Narayan and Middleton (1994) simulated a discretized version of Eq. (5) for CDW depinning

in one to three dimensions. The random force is given by $\eta(\mathbf{r}, \varphi) = V \sin(\varphi - \beta(\mathbf{r}))$, where V is the strength of the pinning force, and $\beta(\mathbf{r})$ is the preferred phase at site $\mathbf{r}$, chosen randomly from site to site. Values of critical exponents as determined in their numerical work are given in Table 1, which show good agreement with the analytic results in section “Analytical Treatments of the Depinning Transition and Universality”. The exponent ν_f (second row) is determined from quantities related to the avalanche propagation below the depinning threshold.

Leschhorn (1993) carried out large-scale simulations of a discretized version of the LIM. Exponents he obtained are also given in Table 1. These values are in good agreement with more recent studies (Rosso et al. 2003). Note that the roughness exponent ζ for a one-dimensional interface at the depinning threshold is greater than one. This gives rise to a subtlety in using Eq. (7) to measure ζ as discussed in (Leschhorn and Tang 1993).

Analytical Treatments of the Depinning Transition and Universality

The depinning transition differs from the usual critical phenomena in thermal equilibrium systems in terms of the vast separation of fast and slow time scales. Therefore the successful development of a renormalization group theory in the early 1990s to effectively capture this unique feature was an important milestone in the analytical studies of nonequilibrium phase transitions. The work acquired broader significance due to the later discovered correspondence between depinning and sand pile models of self-organized

criticality (SOC), which we discuss in section “Self-Organized Criticality”.

Mean-Field Theory

Fisher (1985) and others (Koplik and Levine 1985; Leschhorn 1992; Leschhorn et al. 1997; Narayan and Fisher 1992) considered a mean-field approximation to Eq. (5) which can be treated analytically. It is instructive to examine the calculation in some detail here as the solution reveals several important features of the depinning transition which extend to lower dimensions, while the mathematical manipulations can be kept at an elementary level.

In sufficiently high dimensions, one may approximate the Laplacian in Eq. (5) by a spring force, whose equilibrium point is set by the mean interface position $\bar{u}(t)$. The resulting dynamical equation for a given site on the interface takes the form,

$$du/dt = \gamma(\bar{u} - u) + \eta(u) + F. \quad (10)$$

For simplicity we have dropped μ in (5) through a redefinition of t . In the steady-state, $\bar{u} = vt$, where v is the interface velocity to be determined self-consistently from the solution of Eq. (10). Since the disorder $\eta(u)$ is uncorrelated along the interface, the system-wide average $\bar{u}$ can be replaced by an average over the distribution of $\eta(u)$.

Following the discussion in (Leschhorn et al. 1997), we adopt a moving frame and define $x = u - vt - (F - v)/\gamma$ to be the displacement away from the equilibrium position when the random force $\eta(u)$ is absent. In terms of x , Eq. (10) reads (after a rigid translation of $\eta(u)$),

Collective Transport and Depinning, Table 1 Scaling exponents at the depinning transition. Numbers in parentheses indicate uncertainties in the last digit

	Interface ^a			CDW			MF $D \geq 4$
	$D = 1$	$D = 2$	$D = 3$	$D = 1$	$D = 2$	$D = 3$	
ζ (roughness)	1.25(1)	0.75(2)	0.35(1)	0			0
z (dynamic)	1.42(4)	1.56(6)	1.75(15)	1	1.32(4) ^b	1.65(6) ^b	2
ν, ν_f (correlation length)	1.33(2)	0.80(1)	0.606(4)	0.4(1) ^c 2.01(2)	0.5(1) ^c 0.98(3) ^b	0.5(1) ^c 0.68(4) ^b	1/2
θ (velocity)	0.25(3)	0.64(2)	0.84(2)	0.45(5) ^c	0.64(3) ^{b,c}	0.81(3) ^{b,c}	1

^aLeschhorn (1993); ^bMiddleton and Fisher (1993); Narayan and Middleton (1994); ^cMayer and Sethna (1993)

$$dx/dt = -\gamma x + \eta(vt + x). \quad (11)$$

The self-consistency condition becomes,

$$\gamma \langle x \rangle = -F + v. \quad (12)$$

The driving force F now disappears from the equation of motion (11) and can be computed from (12) as a function of v , once a solution to (11) is found.

As illustrated in Fig. 3, Eq. (11) describes the dynamics of an overdamped particle in a moving potential,

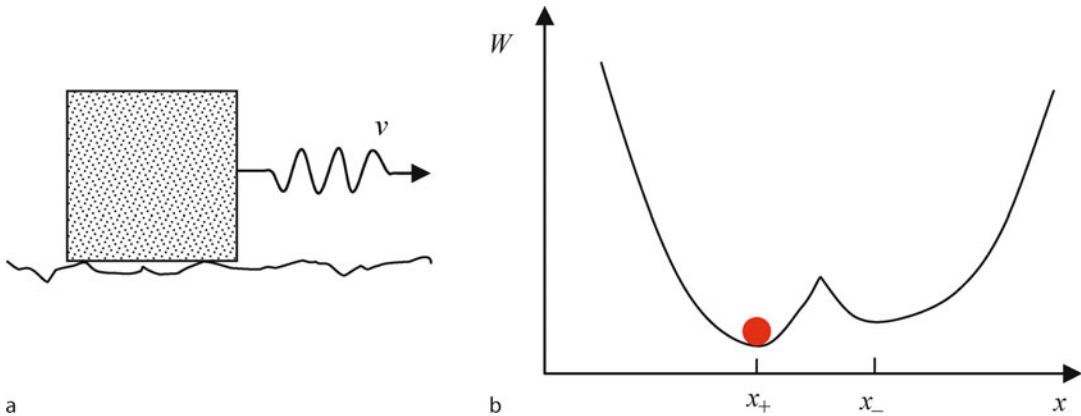
$$W(x, t) = \frac{\gamma}{2}x^2 + U(vt + x). \quad (13)$$

The random part $U(vt + x) = -\int_{x_0}^{vt+x} \eta(u) du$ travels at a constant velocity v to the left or to the right depending on the sign of v . In the quasi-static limit $v \rightarrow 0$, the particle stays in a local minimum of the potential W for the whole time, and is interrupted occasionally by jumps when the minimum it follows disappears. When the potential travels to the left ($v > 0$), the particle traces the leftmost minimum x_+ of W .

The opposite occurs when the potential travels to the right.

With the above picture in mind, we may use Eq. (12) to calculate the thresholds $F_c^+ = -\gamma \lim_{v \rightarrow 0+} \langle x \rangle$ and $F_c^- = -\lim_{v \rightarrow 0-} \langle x \rangle$ for forward and backward depinning, respectively. For a continuous, slow-varying function $\eta(u)$ with a sufficiently small amplitude, the potential W has a unique minimum all the time, and hence $F_c^+ = F_c^- = 0$, i.e., the system is never pinned. However, for a discontinuous function $\eta(u)$ (or for sufficiently strong disorder), the potential W has, from time to time, more than one minimum, and hence $F_c^+ = -F_c^- > 0$. Note that only upward jumps in η (i.e. a sudden weakening of the pinning force) give rise to upward cusps in the potential which generate double minima in W .

When the potential $W(x, t)$ travels at a small but finite velocity v , the ball shown in Fig. 3b is displaced to the leftmost minimum of W by an amount proportional to v due to viscosity. From Eq. (12) and the value of F_c determined above, one finds $v = a(F - F_c)$, where a is a numerical constant. This behavior is confirmed by exact solution of a “two-state” model for the pinning force (Leschhorn 1992). The mean-field velocity exponent is thus given by $\theta_{MF} = 1$.



Collective Transport and Depinning, Fig. 3 The mean-field model of depinning. (a) Block (representing the interface) dragged by a spring whose right end moves at a slow but constant velocity v . The block is sitting on a rough surface and immersed in a very viscous fluid, so that inertia effects can be neglected. (b) The effective potential W on the block at a particular instant when viewed in a

co-moving frame. W is a sum of two parts: A quadratic spring potential plus a random potential U which travels slowly to the left. In the absence of thermal motion, the block (represented by the red ball in the figure) traces the left most minima x_+ of W until it disappears, followed by an “avalanche” into the next available minimum

Functional Renormalization Group

Equation (5) has been studied analytically since the 1970s. Earlier attempts by Efetov and Larkin (1977) and others (Feigel'man 1983; Koplik and Levine 1985) based on a perturbative expansion of the noise term around a flat reference state ran into divergences for $D < D_c = 4$, which can not be cured with the usual renormalization group (RG) procedure. Breakthroughs were achieved in 1992 by Narayan and Fisher (1992) for the CDW depinning and by Nattermann et al. (1992) for the driven interface. In the field theory jargon, the model has an infinite number of relevant operators that correspond to the coefficients in a power-law expansion of the random force correlator $\Delta(u)$. Upon momentum shell integration on a running scale L , the one-loop corrections to these coefficients can be summarized in terms of a functional RG flow for $\Delta(u)$,

$$\frac{d\Delta(u)}{d \ln L} = -cL^\varepsilon \frac{d^2}{du^2} \times \left[\frac{1}{2} \Delta^2(u) - \Delta(u)\Delta(0) \right]. \quad (14)$$

Here $\varepsilon = 4 - D$ and c is a constant. Dependence on L can be absorbed with the scaling transformation $u \rightarrow L^\zeta u$, $\Delta \rightarrow L^{2\zeta-\varepsilon} \Delta$. The resulting flow equation has an infinite number of fixed points, which are distinguished by the number of nodes of the function Δ . Figure 4 shows two such solutions, the first with no node at $\zeta = \varepsilon/3$, and the second with infinitely many nodes (periodic) at $\zeta = 0$. The periodic fixed point is associated with the CDW depinning transition. The one with no node

describes the interface depinning transition. The most prominent feature of the fixed point function Δ^* is the cusp singularity at $u = 0$, which is responsible for the failure of previous RG treatments.

Equation (14) is supplemented with a RG equation for the mobility μ that determines the dynamical response on scale L ,

$$\frac{d \ln \mu}{d \ln L} = -c\Delta''(0+)L^\varepsilon. \quad (15)$$

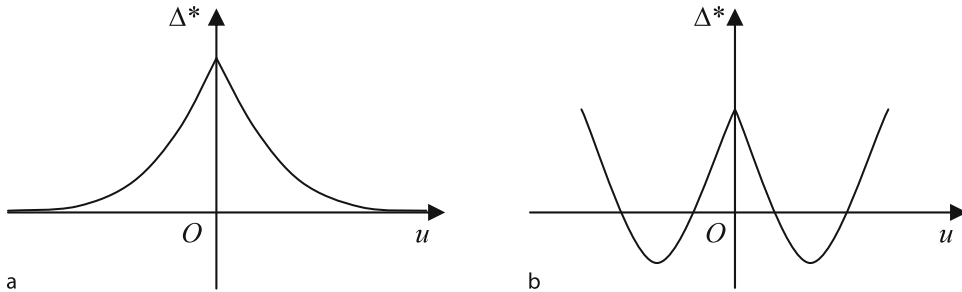
The elastic constant γ , on the other hand, is not renormalized. The latter property yields the scaling relation

$$v(2 - \zeta) = 1. \quad (16)$$

The functional RG analysis has been carried out to two-loop order by Le Doussal and collaborators (Chauve et al. 2001; Le Doussal et al. 2002). This study is particularly useful as it helps to clear up several subtleties which can not be easily resolved in the one-loop calculation. For interface depinning, exponents up to the second order in ε are given by,

$$\begin{aligned} \zeta &= \frac{1}{3}\varepsilon + 0.047771\varepsilon^2 \\ z &= 2 - \frac{2}{9}\varepsilon - 0.0432087\varepsilon^2 \\ v &= \frac{1}{2-\zeta} = \frac{1}{2} + \frac{1}{12}\varepsilon + 0.0258316\varepsilon^2 \\ \theta &= v(z - \zeta) = 1 - \frac{1}{9}\varepsilon + 0.040123\varepsilon^2. \end{aligned} \quad (17)$$

Good agreement is seen with the numerical values given in Table 1.



Collective Transport and Depinning, Fig. 4 Fixed point solutions to Eq. (14) for (a) the linear interface models and (b) the charge-density wave depinning

For CDW depinning, the two-loop analysis yields the following exponents,

$$\begin{aligned}\zeta &= 0 \\ z &= 2 - \frac{1}{3}\varepsilon - \frac{1}{9}\varepsilon^2 \\ v &= \frac{1}{2-\zeta} = \frac{1}{2} \\ \theta &= v(z - \zeta) = 1 - \frac{1}{6}\varepsilon - \frac{1}{18}\varepsilon^2.\end{aligned}\quad (18)$$

Interestingly, here the expression for the dynamical exponent z truncated at first order in ε appears to be in better agreement with the simulation results given in Table 1.

Very recently, Rosso et al. (2007) proposed and implemented a scheme to measure numerically the effective pinning force and the renormalized correlator Δ on large distances. The idea is similar to the mean-field model discussed above, with the particle replaced by the center of mass of the manifold in a weak confining potential that introduces a running cut-off to spatial correlations. Their numerical results provide direct confirmation of the cusp singularity in Δ , which has become the hallmark of the RG theories for the manifold problem.

Contact Line Depinning

The above analysis has been extended by Ertas and Kardar (1994b) to the contact line depinning problem. The increase in surface free energy (or surface area) due to a deformation of the contact line from an ideal straight configuration has been worked out previously by Joanny and de Gennes (1984). Result of this analysis, generalized to a “contact manifold” with D internal dimensions, is that the Laplace term in Eq. (5) is replaced by a nonlocal term, $\gamma \nabla^2 u \rightarrow \int d^D \mathbf{r}' K_D(\mathbf{r} - \mathbf{r}') [u(\mathbf{r}', t) - \bar{u}(t)]$. Here $\bar{u}(t)$ denotes the mean displacement. The function $K_D(\mathbf{r}) \sim |\mathbf{r}|^{-D-1}$ describes the decay of the long-ranged elastic coupling along the contact manifold, assuming the modes in the “bulk” have relaxed. This form of elastic coupling changes the critical dimension to $D_c = 2$. In terms of $\varepsilon = 2 - D$, the critical exponents of the depinning transition from a two-loop renormalization group

calculation by Le Doussal et al. (2002) are given by,

$$\begin{aligned}\zeta &= \frac{1}{3}\varepsilon + 0.13245\varepsilon^2 \\ z &= 1 - \frac{2}{9}\varepsilon - 0.1132997\varepsilon^2 \\ v &= \frac{1}{2-\zeta} = 1 + \frac{1}{3}\varepsilon + 0.24356\varepsilon^2 \\ \theta &= v(z - \zeta) = 1 - \frac{2}{9}\varepsilon - 0.1873737\varepsilon^2.\end{aligned}\quad (19)$$

Interestingly, the same long-range coupling is found to describe tensile crack propagation (Ramanathan and Fisher 1998). Numerical simulations (Duemmer and Krauth 2007) of a discretized long-range model in $D = 1$ ($\varepsilon = 1$) yield $\zeta = 0.385(5)$, $z = 0.770(5)$, $v = 1.625(10)$, $\theta = 0.625(5)$, in good agreement with the theory.

Self-Organized Criticality

Close to the depinning threshold, motion of the system is intermittent. The growth activities are highly localized and exhibit strong correlations over time. The natural separation of slow and fast events at the onset of depinning invites comparison to models of self-organized criticality (SOC) and of earthquakes, which were made popular through the seminal work of Bak, Tang and Wiesenfeld (BTW) (Bak et al. 1987; Bak et al. 1988) on the “sandpile” model. This observation prompted a number of detailed investigations of the microscopic processes leading to the build-up of spatiotemporal correlations as the depinning threshold is approached from below, as summarized in (Paczuski et al. 1996). Subsequent work by several groups (Narayan and Middleton 1994; Paczuski and Boettcher 1996) established a direct link between these two classes of models. This development has also contributed to a better understanding of SOC in automaton models. It opens the door to a systematic exploration of their scaling properties which were hitherto hindered by the lack of a suitable continuum representation.

The mapping between depinning and SOC automaton models is most easily understood by

considering $u(\mathbf{r}, t)$ in Eq. (5) as the accumulated activity of a given lattice site $\mathbf{r}$ after time t (Paczuski and Boettcher 1996). Take for example the original sand-pile model introduced by BTW on a square lattice. The system is specified by an integer height $z(x, y)$ on each lattice site (x, y) . Starting from a random set of values $z_0(x, y)$, “sand” is gradually added through a sequence of events $z(x, y) \rightarrow z(x, y) + 1$, each time only a single site is chosen randomly from all available sites in the system for updating. If the operation leads to an overflow, i.e., $z(x, y) > K$, then toppling takes place according to the rule,

$$\begin{aligned} z(x, y) &\rightarrow z(x, y) - 4 \\ z(x \pm 1, y) &\rightarrow z(x \pm 1, y) + 1 \\ z(x, y \pm 1) &\rightarrow z(x, y \pm 1) + 1. \end{aligned} \quad (20)$$

This process is continued until no site has a height exceeding K . Let $u(x, y; t)$ be the total number of toppling events at site (x, y) from the beginning of the process. Counting the number of sand grains received and given away by the site yields immediately

$$\begin{aligned} z(x, y; t) &= z_0(x, y) - 4u(x, y; t) + u(x + 1, y; t) \\ &\quad + u(x - 1, y; t) + u(x, y + 1; t) \\ &\quad + u(x, y - 1; t) \\ &= z_0(x, y) + \nabla^2 u, \end{aligned} \quad (21)$$

where ∇^2 is the Laplace operator on the lattice. The condition $z(x, y; t) > K$ for toppling $u \rightarrow u + 1$ is thus equivalent to

$$\nabla^2 u + z_0(x, y) - K > 0. \quad (22)$$

The above growth rule is almost identical to a lattice automaton model introduced by Narayan and Middleton (1994) for CDW depinning. Comparing (22) to Eq. (5), we see that here (i) u is restricted to take only integer values plus a random, site dependent shift $\beta(\mathbf{r})$, which can be considered as the preferred phase set by the local disorder; (ii) The dynamical rules obey a global symmetry $u \rightarrow u + 1$, as in CDW depinning. The

usual wisdom in critical phenomena suggests that the two models are in the same universality class due to property (ii), while property (i) is a microscopic detail which does not affect the scaling properties at the depinning transition. Indeed, various scaling exponents determined through analytical and numerical studies of the two models are shown to be consistent with each other (Narayan and Middleton 1994; Tang and Bak 1988). Subtle differences exist, however, in the way the system is driven to criticality (Narayan and Middleton 1994; Paczuski et al. 1996). The effect of boundary conditions also need to be treated with care (Narayan and Middleton 1994).

To eliminate inertia effects in real sand pile avalanches (Nagel 1992) which prevented direct comparison with the BTW model, the Oslo group (Christensen et al. 1996) designed a two-dimensional rice pile experiment that displays power-law scaling and self-organized criticality. The group also proposed an automaton model, known as the Oslo model, which yields critical exponents in good agreement with the experiment. The Oslo model differs from the BTW model only in the choice of the threshold value K for toppling: Instead of taking a constant value, K is site-dependent. Its value is updated after each toppling event at the site. Consequently, condition (22) changes to,

$$\nabla^2 u + z_0(\mathbf{r}) - K(\mathbf{r}, u) > 0. \quad (23)$$

The symmetry $u \rightarrow u + 1$ is no longer present. A similar discussion as above links the Oslo rice-pile model to the LIM of depinning (Bonachela et al. 2007; Paczuski and Boettcher 1996). Other SOC models, such as the Manna model (Manna 1991) and the Zaitsev model (Zaitsev 1992), have similar updating rules as the Oslo model and hence belong to the LIM universality class as well. The mechanism of self-organization and the development of spatiotemporal correlations in the SOC and depinning models have been discussed in detail by Paczuski et al. (1996), who have also identified a large number of scaling relations that give all other exponents in terms of two basic ones.

As an example, let us consider the power-law distribution of the avalanche size which can be measured, e.g., by the total number of toppling events s when a new grain is added. For a system of linear size L , the distribution satisfies the finite-size scaling,

$$P(s, L) = s^{-\tau} F(s/L^\delta). \quad (24)$$

The mapping discussed above identifies $\delta = D + \zeta$, i.e., the dimension of the total volume swept by the interface in a system-wide avalanche. On the other hand, a sum rule yields the following expression,

$$\tau = 2 - \frac{\zeta + \nu^{-1}}{\zeta + D} \quad (25)$$

For example, the exponents $\zeta = 0$ and $\nu = 1/2$ for the CDW depinning predicts $\tau = 2(D-1)/D$, in excellent agreement with simulation results on the sandpile model in two and three dimensions (Tang and Bak 1988). Care must be taken, however, in applying Eq. (25) to the $D = 1$ rice pile model in the boundary driven case, as noted by Paczuski and Boettcher (1996).

Interface Depinning in Anisotropic Medium

Easy and Hard Directions of Depinning

The linear interface model defined by Eq. (5) together with Eq. (6) for the random force is statistically invariant under the *tilt transformation* $u \rightarrow u + \mathbf{s} \cdot \mathbf{r}$, where $\mathbf{s}$ is the slope of the interface. Hence the depinning threshold F_c , as well as other critical properties, are independent of the orientation of the interface. This property holds for an interface moving in an isotropic medium.

When the medium is anisotropic, one or more of the model parameters that enter the estimate Eq. (4) for F_c may change with $\mathbf{s}$. Consequently, the depinning threshold $F_c(\mathbf{s})$ becomes orientation-dependent (Tang et al. 1995). An interface oriented in the “easy” direction enters the moving phase at the weakest driving. However, a moving interface in this direction is

generically unstable against faceting towards directions of slower growth, particularly near the depinning threshold. To illustrate this point, we may consider a part of the interface that is slowed down by an exceptionally strong pin. As the rest of the interface moves forward at a higher velocity, a local tilt develops that moves the interface away from the easy direction. This further strengthens the pinning effect, producing a cone-like structure. Indeed, the depinning transition in the easy direction has been shown to be of first order with a velocity jump (Jeong et al. 1996).

The story is different for an interface oriented in the “hard” direction. Both numerical (Amaral et al. 1994, 1995; Buldyrev et al. 1992a; Tang and Leschhorn 1992) and experimental (Amaral et al. 1995; Buldyrev et al. 1992a, b) studies have shown that the depinning transition here is continuous, but the critical exponents take different values from those of the LIM. Yet another set of critical exponents are encountered when the interface is forced to tilt away from the hard direction by, say boundary conditions (Tang et al. 1995). The resulting depinning problem is related to *directed percolation*, which we consider in some detail below.

A Lattice Automaton

Tang and Leschhorn (1992) introduced a lattice automaton for imbibition in a two-dimensional porous medium. A very similar model was studied by Buldyrev et al. (1992a) around the same time and reported together with experimental results. The automaton model is defined as follows. On a square lattice, each site (i, j) is assigned a random pinning force $\eta(i, j)$, uniformly distributed in the interval $[0, 1)$. At $t = 0$, the interface h_i is completely flat. In each time step, growth $h_i \rightarrow h_i + 1$ is performed in parallel when either of the following two conditions is satisfied: (i) the random force $\eta(i, h_i)$ on the interface at column i is less than a pre-specified driving force f ; or (ii) $h_i < h_{i-1} - 1$ or $h_i < h_{i+1} - 1$. Thus to obtain a completely pinned interface, we must have $|h_i - h_{i-1}| \leq 1$ and $\eta(i, h_i) > f$ (called a blocking site) for all i . This condition requires the existence of a *directed percolating path* through blocking sites. Such paths exist if the density p of blocking sites exceeds a critical

Collective Transport and Depinning, Table 2 Summary of the exponents for directed percolation depinning along the hard direction. After (Amaral et al. 1995)

	$D = 1$	$D = 2$	$D = 3$	$D = 4$	$D = 5$	$D = 6$	MF
ζ (roughness)	0.63(1)	0.48(3)	0.35(1)	0.27(5)	0.25(5)	0.2(2)	0
z (dynamic)	1	1.15(5)	1.36 (5)	1.58(5)	1.7(1)	1.8(2)	2
ν (correlation length)	1.73(2)	1.16(5)	0.95(10)	0.66(10)	0.6(1)	0.5(1)	1/2
θ (velocity)	0.58(7)	0.8(2)	1.0(2)	1.0(2)			1

value $p_c \simeq 0.539$. Consequently, the depinning threshold is given by $f_c = 1 - p_c \simeq 0.461$. It is possible to show that, for $f < f_c$, the interface stops at the first directed percolating path that lies fully above its initial position.

The roughness of the incipient directed percolating path at $p = p_c$ is $\zeta = v_\perp/v_\parallel \simeq 0.63$, where $v_\parallel = 1.733$ and $v_\perp = 1.097$ are exponents that characterize the divergence of parallel and perpendicular correlation lengths, $\xi_\parallel \sim |p - p_c|^{-v_\parallel}$, $\xi_\perp \sim |p - p_c|^{-v_\perp}$, respectively [41]. This is also the roughness exponent assumed by the interface at the depinning threshold $f = f_c$. Simulations (Tang and Leschhorn 1992) have shown that the dynamic exponent $z = 1$ at the depinning transition of the above model, while the crossover length exponent $\nu = v_\parallel$. From Eq. (8) one obtains $\theta = v_\parallel - v_\perp \simeq 0.63$.

The orientational dependence of the depinning threshold in the automaton model has been studied by applying the helical boundary condition $h_{i+L} = h_i + sL$ which forces a global tilt (Tang et al. 1995). The threshold force is indeed found to be lower. This behavior matches well with the well-known property of directed percolation: For $p > p_c$, percolating paths fall within a cone of opening angle $\varphi(p)$ around the symmetry direction (Kinzel 1982). If the average tilt s of the interface exceeds this angle, no spanning percolating path exists and the interface is free to move. The roughness exponent of the cone boundary is $\zeta = 1/2$, which belongs to yet another universality class of interface depinning away from a symmetry direction (Tang et al. 1995).

The above automaton model has been generalized by Buldyrev et al. (1992b) to higher dimensions. The directed percolating strings are replaced by directed percolating surfaces which have been considered in the context of resistor-

diode percolation (Dhar et al. 1981). The roughness exponent of such a surface at the percolation threshold in $D = 1$ dimensions is given in Table 2. Havlin et al. (1995) investigated in detail the temporal sequence of growth activities at the depinning transition, which exhibits an interesting super-diffusive behavior. They argued that the dynamic exponent z that describes the growth in size of the affected region after an initial depinning event is related to the scaling of minimal path length with Euclidean distance on the critical (isotropic) percolation cluster in D dimensions. The values of z from their work are also given in Table 2.

As in the $1 + 1$ dimensional case, a tilted interface has a lower depinning threshold. Just above the depinning threshold, the interface decomposes into stripes of inactive regions perpendicular to the tilt, separated by active fronts that propagate towards the “easy” direction at a finite velocity. Based on this phenomenology, Tang et al. (1995) determined exponents characterizing the depinning transition of a tilted interface. In particular, the velocity exponent $\theta = 1$ in all dimensions.

Quenched KPZ Equation

The slope-dependent depinning threshold can be modeled explicitly by adding the Kardar–Parisi–Zhang (KPZ) term to Eq. (5). The resulting equation of motion takes the form,

$$\mu^{-1} \frac{\partial u}{\partial t} = \gamma \nabla^2 u + \frac{1}{2} \lambda (\nabla u)^2 + \eta(\mathbf{r}, u) + F. \quad (26)$$

In the original proposal (Kardar et al. 1986), the λ -term is due to a kinematic effect known as lateral growth, and hence its strength is proportional to the interface velocity v . At the depinning

threshold, however, this term is present only when the medium is anisotropic. A positive λ describes depinning along a hard direction, while a negative λ corresponds to growth along an easy direction. Directed numerical integrations (Csahók et al. 1993; Leschhorn 1996) of Eq. (26) in $(1 + 1)$ dimensions yielded exponents consistent with the directed percolation models. The relevance of the KPZ nonlinearity in modifying the critical behavior of the LIM has also been confirmed by renormalization group calculations (Le Doussal and Wiese 2003; Stepanow 1995).

Future Directions

Through the intensive work by many groups in the past 15 years, the depinning transition of elastic manifolds in a disordered medium has emerged as one of the best understood nonequilibrium critical phenomena with nontrivial scaling properties. The discovery of a renormalizable continuum theory provided the much needed theoretical foundation for the identification of universality classes and symmetry principles. Owing to this remarkable development, models and experimental systems that differ in microscopic details can be compared and classified with regard to their threshold behavior. More recent refinements of the theory by the Paris group (e.g., Le Doussal et al. 2008) have yielded deeper insights on the role of the cusp singularity of the random force correlator in capturing the multiple-minima energy landscape of the disordered manifold problem.

Within the class of models describe by Eq. (5), there are still a few unresolved issues. For example, the roughness exponent ζ of the $(1 + 1)$ -dimensional LIM has been found numerically to be indistinguishable to $5/4$, suggesting the possibility of an exact derivation. The effect of a thermal noise term added to the deterministic model has not been well-understood (Bustingorry et al. 2008; Middleton 1992b; Vandembroucq et al. 2004). There now exist very good numerical estimates of the exponent ψ that describes the vanishing of the interface velocity $v \sim T^\psi$ with temperature T at the depinning threshold, but its

value does not agree with any of the existing theoretical proposals (Bustingorry et al. 2008). Another puzzle is the closeness between the numerical estimates for the dynamical exponent z given in Table 1 and the one-loop RG prediction for the CDW depinning.

The mapping between the CDW depinning and the sandpile models offers a very powerful tool for the development of RG theories for systems that exhibit SOC. To our knowledge, this connection has not been fully explored so far. It would be interesting to see if SOC models other than the sandpile and the rice-pile, such as the Olami–Feder–Christensen model (Olami et al. 1992) for earthquakes, can also be mapped to some type of depinning model. Conversely, it would be nice to find out whether the lessons learned from the detailed characterization of avalanche dynamics (Dhar 2006) can contribute to a better understanding of critical correlations in the LIM at the depinning threshold from small to large scales.

On the experimental side, perhaps the best studied system is the CDW depinning, yet the CDW velocity generally grows faster than linear above the depinning threshold (Thorne 2005), while the elastic depinning theory predicts $\theta < 1$. It has been suggested that the apparent discrepancy could be due to a combination of factors: Nonuniform driving, thermal activation across energy barriers, and plasticity when dislocations in the phase field is present. Simultaneous presence of strong pinning sites and weak collective pinning in a finite system may also give rise to a complex I–V curve in experimental systems. While some of these effects have been investigated theoretically (Saunders et al. 2004) (see also the review by Brazovskii and Nattermann), a clear picture is yet to emerge.

Moulinet et al. (2002) designed an experimental system to study the roughness and dynamics of the contact line of a viscous fluid. The roughness exponent ζ obtained from experimental measurements is 0.5, much bigger than the value 0.385 obtained from numerical simulations (Duemmer and Krauth 2007) of the model considered by Ertas and Kardar (1994b). Similar discrepancies have been reported in the experimental studies (Bouchaud et al. 2002; Ponson et al. 2006) of

the roughness of crack fronts. Modifications of the LIM to include nonlinear couplings and wavelike dynamics (Bouchaud et al. 2002) for avalanche propagation have been suggested. However, many unresolved issues remain.

It is perhaps not surprising to see that real physical systems almost always contain complications that invalidate direct comparison with the linear elasticity theory of depinning. The pinned state just below the transition is highly metastable and hence is susceptible to various relaxational processes that could possibly invalidate our simple assumptions (see, however (Kolton et al. 2006) for a discussion of correlation lengths below the elastic depinning threshold). In-homogeneities inside the sample, e.g., macroscopic variations in the concentration of impurity atoms, may also have a dramatic effect on the critical properties associated with the depinning transition. Incorporating the relevant microscopic processes into the generic description discussed here is expected to yield a more complete theory of depinning. It is hoped that future work in this direction will unleash the full impact of the theoretical progress that have been made in the past two decades, which in itself has been intellectually extremely stimulating.

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Disordered Elastic Media

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Article Outline

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Glossary

Pinning An action exerted by impurities on an object. The object has a preferential position in space, and will move in response to an external force only if this force is large enough.

Scaling The fact that each of two quantities varies in a power-law relationship to the other.

Random manifold A single elastic structure (line, sheet) embedded in a random environment.

Bragg glass A periodic elastic structure embedded in a weakly disordered environment, nearly as ordered as a solid but exhibiting some characteristics normally associated with glasses.

Creep Very slow response at finite temperature of a pinned structure in response to an external force.

Definition of the Subject

Many seemingly different systems, with extremely different microscopic physics, ranging from magnets to superconductors, share the same essential ingredients and can be described under the unifying

concept of disordered elastic media. In all these systems, an internal elastic structure, such as an interface between regions of opposite magnetization in magnetic systems, is subject to the effects of disorder existing in the material. A specially interesting feature of all these systems is that these disordered elastic structures can be set in motion by applying an external force on them (e.g. a magnetic field sets in motion a magnetic interface), and that motion will be drastically affected by the presence of the disorder. What properties result from this competition between elasticity and disorder is a complicated problem which constitutes the essence of the physics of disordered elastic media. The resulting physics present characteristics similar to those of glasses. This poses extremely challenging fundamental questions in determining the static and dynamic properties of these systems. Understanding both the static and dynamic properties of these objects is not only an important question from a fundamental point of view, but also has strong practical applications. Indeed, being able to write an interface between two regions of magnetization or polarization, and the speed of writing and stability of such regions, is what conditions, in particular, our ability to store information in such systems, as (for example) recordings on a magnetic hard drive. The physics pertaining to disordered elastic media directly condition how we can use these systems for practical applications.

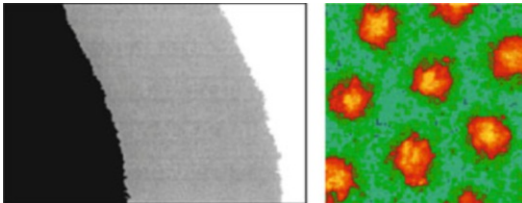
Introduction

Understanding the statics and dynamics of elastic systems in a random environment is a long-standing problem with important applications for a host of experimental systems. Such problems can be split into two broad categories: (a) propagating interfaces such as magnetic (Lemerle et al. 1998; Krusin-Elbaum et al. 2001; Repain et al. 2004; Metaxas et al. 2007), spintronic (Yamanouchi et al. 2006, 2007), or ferroelectric (Tybell et al. 2002; Paruch et al. 2005) domain walls, fluid invasion in porous media (Wilkinson and

Willemsen 1983), contact lines in wetting (Moulinet et al. 2002), epitaxial growth (Barabasi and Stanley 1995) or crack propagation (Bouchaud et al. 2002; Alava et al. 2006); (b) periodic systems such as vortex lattices in type II superconductors (Blatter et al. 1994; Nattermann and Scheidl 2000; Giamarchi and Bhattacharya 2002), charge density waves (Grüner 1988; Nattermann and Brazovskii 2004), magnetic bubbles (Seshadri and Westervelt 1992), colloids (Murray et al. 1990), Wigner crystals of classical particles (Couplier et al. 2005) or of electrons (Andrei et al. 1988; Giamarchi 2004).

Although all these systems have very different microscopic descriptions, one aspect of their physics is identical at a more macroscopic scale: An object exists that obeys a macroscopic elastic description. For case (a) this is an interface separating two different regions of the system, for example in a magnetic material a domain wall separating regions of opposite magnetization. An example of such an interface is shown in Fig. 1. Since creating an interface costs energy, the interface left to itself would tend to be flat, and there is

an elastic cost to its deformations. Since this object lives inside a microscopic crystal with disorder, it is also subjected to potentials that tend to roughen it and pin it in specific regions of space. This interface can be set in motion by applying an external force on it, caused for example by a magnetic field for the magnetic domain wall or an electric field for a ferroelectric. For case (b), that of periodic systems, a similar physics exists. A “crystal” of objects (lines for vortices, points for magnetic bubbles and colloids, or sheets for charge-density waves) exists inside the system. Since these objects repel each other, in the absence of disorder they would tend to form a perfect periodic crystal. In a way similar to the interfaces, such crystals can be set in motion by applying an external force (for example a current, in the case of vortices). The disorder present at the microscopic level tends to pin this crystal. It is important to note that one is dealing here with the physics of a crystal embedded in an external medium containing impurities. The disorder can thus vary at a length scale much smaller than the lattice spacing of the moving crystal, which leads to a physics radically novel compared to that of chemical impurities in a regular solid. Understanding the physics, both static and dynamic, of these objects has thus been a considerable challenge in the last 50 years or so. There are several reasons for pursuing this interest, and for tackling the challenges posed by this field of disordered elastic media.



Disordered Elastic Media, Fig. 1 Left: an interface in a magnetic system separating two different magnetic polarizations (dark and white). The image is $90 \times 72 \mu\text{m}^2$. The roughness of the domain wall due to the presence of disorder in the system is obvious on the image. Two positions of the interface are shown. Dark and gray correspond to two consecutive images after the interface has been pulled to the right by applying a magnetic field to the sample favoring the magnetization direction on the left of the interface. Such a magnetic field acts as a force pulling the domain wall. [From Lemerle et al. 1998 (Copyright 1998 by the American Physical Society)]. Right: A vortex lattice image, from Scanning Tunneling Microscope, in the superconductor MgB_2 . The tips of the vortices on the surface of the sample are shown in the image, and correspond to the red parts. The image is about 250nm^2 . In a perfectly pure system, the vortex lattice is a periodic arrangement (here in a triangular lattice) of objects of a given size (here the core size of the vortex). Disorder affects this perfectly periodic arrangement over a large distance. [From Eskildsen et al. 2002 (Copyright 2002 by the American Physical Society)]

First, at the fundamental level these systems pose difficult and important questions. It has been known since the 1970s that the presence of disorder is crucial (Larkin 1970) and changes the physics completely. While the resulting models are very difficult to solve, they have contributed to pushing the limits of our understanding of disordered systems, and to developing new techniques of statistical physics to deal with such issues. In particular, it is clear that from the competition between disorder and elasticity emerges a complicated energy landscape with many metastable states. This results in glassy properties (Mézard et al. 1987) such as hysteresis and history dependence of the static configuration. Initially viewed as toy models of glasses, these systems have

acquired their own importance and have posed their own challenging questions. Understanding the static properties of such systems has stimulated the development of sophisticated approaches such as replica theory (Mézard and Parisi 1991), functional renormalization groups (Fisher 1986) and numerical methods. Much progress has recently been accomplished due to both analytical and numerical advances. If the static view allows us to improve our techniques of statistical physics, the dynamic view is even more complicated since most of our theoretical tools fail. These systems thus provide wonderful motivations to develop new techniques to tackle the out-of-equilibrium dynamics of disordered systems and to understand and unify the concepts of out-of-equilibrium physics of glasses.

Second, in addition to this theoretical motivation, the ability to apply these concepts in so many different physical systems is a tremendous motivation and challenge. The various realizations allow us to apply stringent tests to proposed theories and, as we will see, have very often served to kill misguided proposals or to put the theory on the right track in these quite complicated systems. Experiments in these systems can be remarkable by the range they offer. In vortex systems, for example, one can vary the vortex lattice spacing by several orders of magnitude just by changing the magnetic field applied to the sample, something impossible to do on a simple crystal. Similarly, for magnetic domain walls, measurements of the velocity in response to an external force can span about ten orders of magnitude. This interplay and exchange between theory and experiment has fueled the field and contributed greatly to its progress.

Last but not least, the phenomena studied for disordered elastic media have a potential impact for applications. Creating interfaces in magnetic or, more recently, ferroelectric materials is a way to store information (with “0” being one direction of magnetization or polarization and “1” being the reverse). This idea is at the root of information storage in a magnetic hard drive or in ferroelectric or magnetic bubble memory. How well one can store the information is thus directly related to both the static and dynamic properties of such interfaces. In particular, stability of the written

information is ensured only if the interface is pinned and will not meander due to outside forces, such as thermal agitation. Similarly, there has been much interest recently on spintronic materials where the magnetic properties can be manipulated by applying electrical currents (Yamanouchi et al. 2006; Yamanouchi et al. 2007). In the same vein, multiferroic materials (Nature Group 2007) allow manipulation of ferroelectric properties by the application of magnetic fields. How the disordered interfaces behave in such materials will certainly determine their possible use for information technology. In a similar way, the vortex lattice in a superconductor is set in motion by the application of a current, while its motion generates a voltage. The dynamic properties of the vortex lattice, and how well it is pinned, thus directly affect the absence of resistance of a superconductor (Blatter et al. 1994; Nattermann and Scheidl 2000; Giamarchi and Bhattacharya 2002), hence its potential uses. Other examples, such propagation of fractures, clearly show the potential importance of such phenomena for applications.

This chapter presents basic concepts and results in this very active field. Section “[Interfaces and Basic Concepts](#)” presents the basic concepts and discusses the static properties of interfaces and domain walls. Section “[Periodic Systems and Bragg Glass](#)” deals with the periodic systems and their differences compared to interfaces. Section “[Pinning and Dynamics](#)” presents concepts and important questions for the dynamics of disordered elastic media, with focus on depinning in section “[Depinning](#)”, on large velocity behavior in section “[High Velocity Phase](#)” and responses to small external forces in section “[Small Applied Force and Creep Motion](#)”. Finally, section “[Future Directions](#)” discusses future directions of and perspectives on the field.

Static Properties of Disordered Elastic Media

Interfaces and Basic Concepts

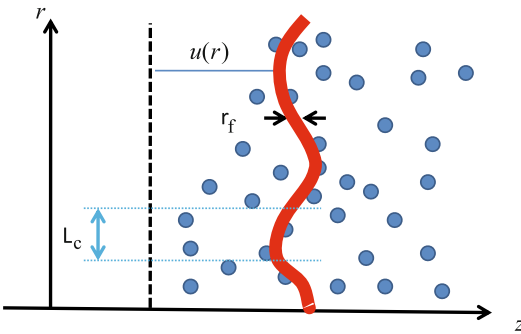
This section introduces the basic ingredients of the systems under study and discusses the specific case of interfaces. An interface is a sheet of dimension

d living in a space of D dimensions. For realistic interfaces $D = d + 1$, but generalizations are of course possible. If we let r represent the internal coordinate of the interface and z all its transverse directions, the interface position is described by displacement $u(r)$ from a flat configuration. This totally determines the shape of the interface provided that u is univalued, i.e., that there are no overhangs or bubbles. The modelization of a one dimensional interface ($d = 1$) in a two dimensional film is shown in Fig. 2.

Since interface distortions cost elastic energy, a system's zero temperature equilibrium configuration in the absence of disorder is flat. Deviations from this equilibrium position are described by a Hamiltonian $H[u]$ which is a function of the displacement u . For small displacements one can make the usual elastic approximation

$$H[u] = \frac{1}{2} \int \frac{d^d q}{(2\pi)^d} c(q) u_q^* u_q, \quad (1)$$

where u_q is the Fourier transform of $u(r)$ and $c(q)$ are the so-called elastic coefficients. If the elastic



Disordered Elastic Media, Fig. 2 A one dimensional interface (such as a magnetic domain wall), shown in red, living in a two dimensional space (film). The position of the interface is determined (provided there are no overhangs or bubbles) by the displacement $u(r)$ from a flat configuration, indicated by the dashed line. In the absence of disorder, denoted by the blue dots, which pin the line in preferred positions in space, the line would be flat. The competition between elasticity and disorder leads to the physics of disordered elastic media and to glassy properties. The thickness of the line, denoted r_f , or the correlation length of the disorder define the Larkin length L_c for which the relative displacements are of the order of r_f , namely $u(L_c) - u(0) \sim r_f$

forces acting on the interface are short ranged then one has $c(q) = cq^2$ which corresponds to

$$H[u] = \frac{c}{2} \int d^d r (\nabla u(r))^2. \quad (2)$$

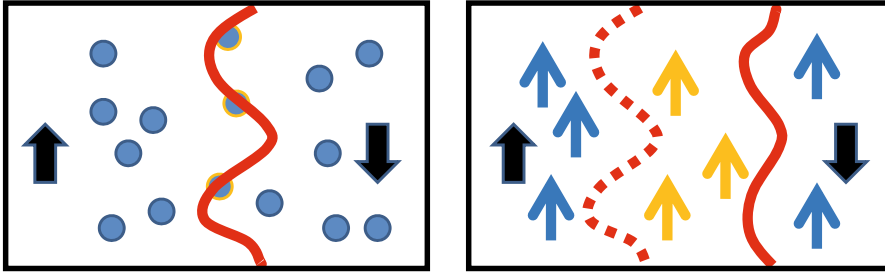
For some interfaces where long range interactions play a role, different forms of elasticity are possible. This is particularly the case when dipolar forces (Nattermann 1983) are taken into account (Paruch et al. 2005) or for the contact line in wetting (Joanny and de Gennes 1984) and crack propagation (Gao and Rice 1989).

In addition to elastic energy, the interface gains some energy by coupling to the disorder. Two universality classes for the disorder exist (see Fig. 3). The random bond disorder corresponds to impurities that directly attract or repel the interface. In contrast, for random field disorder the pinning energy is affected by all the randomness that the interface has encountered in its previous motion. On a more technical level, random bond disorder couples in a symmetric way to the two order parameters on each side of the domain wall, while random field disorder introduces an asymmetry between these two in equivalent order parameters. If $V(r, z)$ denotes the random potential generated by the impurities the pinning energy:

$$H_{\text{dis}}[u] = \int d^d r \begin{cases} V(r, u(r)) & \text{random bond} \\ \int_0^{u(r)} dz V(r, z) & \text{random field.} \end{cases} \quad (3)$$

As is obvious from Fig. 3, even if the microscopic disorder is short-range correlated, as in the case of the random field disorder, the fact that the energy of the system integrates between two positions of the interfaces means that long range correlations exist if one considers the description only in terms of the interface. The full Hamiltonian given by (1) and (3) describes the properties of disordered elastic media, and despite its apparent simplicity hides an extremely rich physics.

The competition between disorder and elasticity manifests itself in several properties of the



Disordered Elastic Media, Fig. 3 The two universality classes of disorder (the names come from the magnetic realization of such systems). In both figures the domain wall in red separates two regions with different order parameters, denoted by the two thick black arrows. Left: random bond disorder. The impurities, denoted in blue, couple symmetrically to the two sides of the domain wall, thus only the impurities on the domain wall (denoted with

the orange circle) contribute to the energy. Right: random field disorder. The impurities, denoted by the blue arrows, favor one of the two sides. Thus, all the impurities (denotes in orange) between two configurations of the domain wall contribute to the energy. This leads to a disorder seen by the domain wall which has long range correlations, even if the microscopic disorder is short-range correlated

interface. From an energetic point of view, this competition leads to a complicated energy landscape for the configurations of the system, with many metastable states leading to glassy properties. The competition also manifests itself in the shape of the interface. In particular, it deviates from the flat configuration and becomes rough. From the scaling of the relative displacements correlation function, a roughness exponent ζ can be defined from the correlation function of the displacements

$$B(r) = \overline{\langle [u(r) - u(0)]^2 \rangle} \propto r^{2\zeta}, \quad (4)$$

where $\langle \rangle$ denotes thermodynamic average and $\overline{\langle \rangle}$ denotes disorder average. There are relations between the shape of the line and the energetic properties. In particular, (4) suggests that displacements would scale with distance as $u(L) \sim L^\zeta$. (2) suggests that the energy of a sample of size L fluctuates from sample to sample as

$$\Delta F(L) \sim L^{d-2+2\zeta}. \quad (5)$$

Given the complexity of the problem, several approximate methods have been put forward to portray the role of disorder. A remarkable model by which to probe the physics of such systems was introduced by Larkin (1970), and goes by the name of the Larkin model. The idea is to focus

on short length scale properties. In that case, the displacements are small and one can expand the disorder term in power of the displacements

$$\begin{aligned} H_{\text{dis}} &= \int d^d r V(r, u(r)) \\ &\simeq \int d^d r [V(r, 0) + \nabla_r V(r, 0)|_{z=0} u(r)]. \end{aligned} \quad (6)$$

The first term is a trivial constant and the second one indicates that the interface is subject to a random force

$$H_L = \int d^d r f(r) u(r). \quad (7)$$

Although this model has several pathologies, it has the advantage of being quadratic in the displacement field u and thus of being exactly solvable. It shows that below $d = 4$, disorder plays a major role. The displacements grow as a function of distance and

$$B(r) = r^{4-d}. \quad (8)$$

This confirms that there is algebraic roughening of the interface with the displacements growing as a power law of distance. One can define the scaling $u(L) \sim L^\zeta$, with the Larkin model giving $\zeta = (4 - d)/2$. Below $d = 4$, disorder is relevant and drastically modifies the physical properties of

the interface compared to those of the non-disordered one. In addition to the exponent itself, since the displacements grow unboundedly, there exists a length scale, L_c , called the Larkin length, at which the displacements become of the order of the only characteristic scale available, namely either the correlation length of the random potential or the size of the interface r_f as shown in Fig. 2. Clearly, this is also the length where the applicability of the Larkin model breaks down, since beyond that length the potential $V(r, z)$ is not smooth anymore and thus expansion in powers of u is not justified. Beyond this length, the system will thus truly feel the effects of random potential. One can thus expect metastability, glassy effects and pinning to appear above that length. One has to determine the physics of this regime appearing above the Larkin length, which we will call the random manifold regime. The Larkin length is thus an important length scale for the static properties since it separates two different regimes for the interface. As I will discuss in section “Pinning and Dynamics”, the Larkin length also has considerable consequences for the dynamics.

To solve the problem in the random manifold regime is not easy and requires greatly sophisticated techniques of statistical physics. To get a rough idea, one can simply use a scaling argument, known as the Flory argument (Blatter et al. 1994). At scale L , the elastic energy scales as $cL^{d-2}u(L)^2$. To estimate the disorder term is more complicated but one can assume that if L is large enough, one sums random variables $V(r, z)$. If one considers for example random bond disorder, because the disorder is short-range correlated, one has

$$\overline{V(r_1, u_1)V(r_2, u_2)} = D\delta^m(u_1 - u_2)\delta^d(r_1 - r_2). \quad (9)$$

Since a $\delta(r)$ function has the dimension of $1/r^d$, this leads to the scaling

$$V(r, u) \sim D^{1/2}u(L)^{-m/2}L^{-d/2}, \quad (10)$$

where m is the number of components of u (for an interface $m = 1$). The disorder term thus scales as

$$H_{\text{dis}} = D^{1/2}u(L)^{-m/2}L^{d/2}. \quad (11)$$

Balancing the elastic and disorder terms leads to a scaling $u(L) \sim L^\zeta$ with $\zeta = \frac{4-d}{4+m}$ for the random bond case and $\zeta = \frac{4-d}{4-m}$ for the random field case. This argument suggests that even in the random manifold, the interface remains rough, with unbounded displacements growing with an *algebraic* roughness. The value of the exponent is characteristic of the universality class of the disorder, and different from the one occurring below $L < L_c$ where the Larkin model applies.

Clearly this simple argument needs to be substantiated by more rigorous calculations. Because the system is subjected to a random potential and the metastability and glassy effects matter, one can use the techniques traditionally used for disordered systems and spin glasses. For a one dimensional interface, this problem can be solved exactly and the roughness exponent $\zeta = 2/3$ obtained (Huse and Henley 1985; Kardar 1985). Note that this exact value is, of course, slightly different from the mean field estimate. In higher dimensions three main methods have been used to tackle this problem. The first one uses the so-called replica trick (Mézard et al. 1987) to average over the disorder and then a variational approach to solve the corresponding field theory (Mézard and Parisi 1991). In this method the initial symmetry between replicas is broken, something familiar in spin-glasses and characteristics of glasses with many metastable minima in the energy. This approximate method gives back the Flory exponent. The second method applies the traditional renormalization technique (RG), so successful for standard critical phenomena. This consists in looking at the problem at larger and larger length scales, eliminating degrees of freedom, while changing the Hamiltonian to ensure that the large length scale physics remain invariant. Usually one can expand the interaction potential, and only a few terms are relevant, which means that the RG consists in the flow of a small number of coupling constants. In the case of disordered elastic systems, the task is considerably more complex since all powers in the expansion of the correlator of the disorder have the same scaling dimension. During the flow the *whole*

correlator of the disorder is modified. One must thus follow the renormalization of a whole function, hence the name functional renormalization group (FRG) (Fisher 1986). This leads to a remarkable property: Beyond a length scale that coincides with the Larkin length, the disorder correlator, initially a smooth analytic function, becomes non-analytic and develops a cusp. The appearance of this non-analyticity is, in this method, the signal of glassy physics. FRG allows us to obtain the roughening exponent in a systematic expansion in $\epsilon = 4 - d$. This has been worked out for the moment up to second order in $\epsilon = 4 - d$, leading to $\zeta = 0.20829804\epsilon + 0.0068582\epsilon^2$ and $\zeta = \epsilon/3$ for the random bond and random field disorder, respectively (Le Doussal et al. 2004). Note that for the random field the mean-field (Flory) exponent is exact due to the long range nature of the disorder. In addition to these analytical approaches, a very useful approach is provided by numerical studies of such systems, using either molecular dynamics simulations (Giamarchi et al. 2006), Monte Carlo techniques (Yoshino 1998; Rosso and Krauth 2002a), or specially designed algorithms (Rosso and Krauth 2002b; Petaja et al. 2006). Numerical approaches are of course quite challenging due to the glassy nature of the system with many metastable minima close to the ground state. However they have proven quite useful in obtaining not only the asymptotic regime but also the full crossover between the Larkin and random manifold regimes, as well as in incorporating the effects of finite temperature.

These predictions can be verified experimentally. I show in Fig. 4 the roughness exponent as measured in a magnetic and a ferroelectric film. The algebraic growth of the correlation function $B(r)$ is clearly seen. These two experimental situations correspond to two different dimensionalities for the domain walls, due to the different thicknesses of the material and different characteristics of the domain wall.

Now we can say that we have a rather good understanding of the static properties of the interfaces, at least for the simple case of local elasticity shown here. Of course even for the statics this is not the end of the story, since several microscopic

systems such as the contact line of a fluid or ferroelectric systems, have long range interactions (dipolar interactions) making even the static properties quite challenging to determine. Other open questions will be discussed in section “Future Directions”.

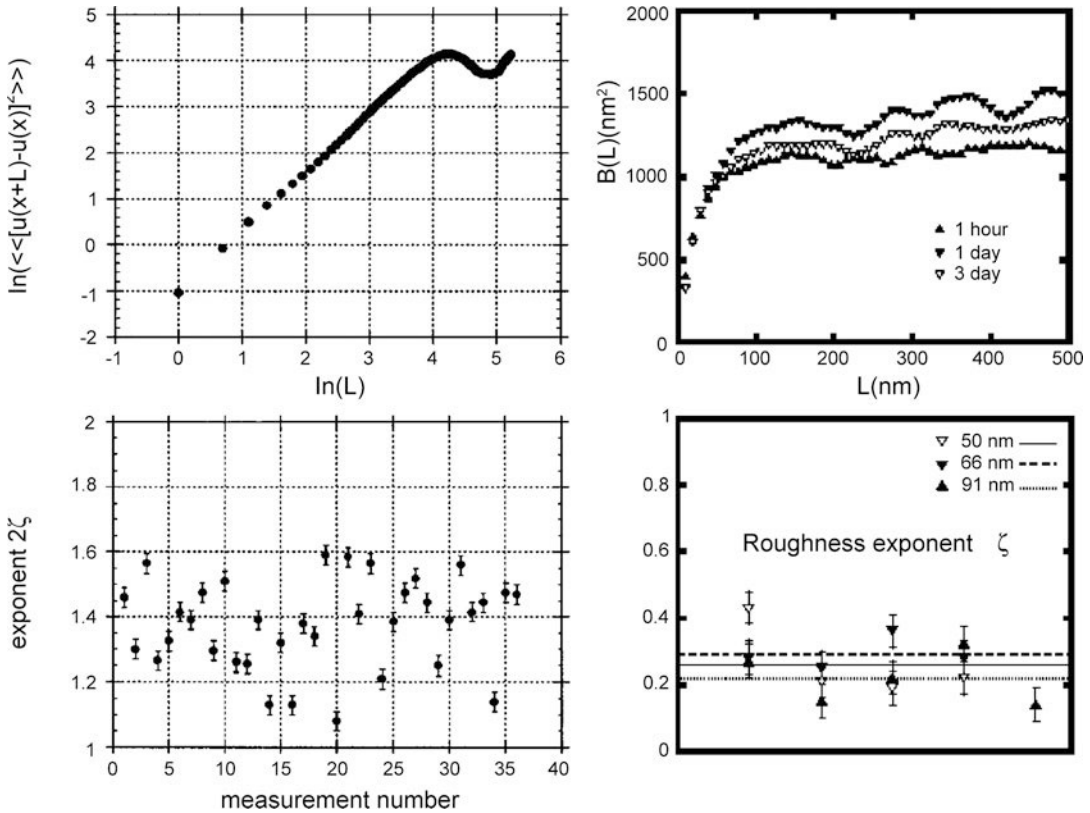
Periodic Systems and Bragg Glass

Similar concepts apply directly to the case of periodic systems. In all these systems the constituent elements (lines for vortices, points for colloids and magnetic bubbles, sheets for phase maxima in the charge density wave systems) form a solid that is embedded into the microscopic system but can have widely different characteristics and, in particular, widely different lattice spacing. For example, in the case of vortices, lattice spacing is controlled by the magnetic field and can easily be varied. An important characteristic is that, in a similar fashion to the interface, this crystal can be embedded in the “external” disorder that corresponds to the imperfections of the real microscopic lattice in which this artificial crystal lives. It is important to note that the variation of the disorder potential can thus occur at length scales much smaller than the lattice spacing.

Each point of the system can be described by an equilibrium position R_i^0 forming a perfect lattice (usually triangular for the vortex lattice), and a displacement u_i relative to this equilibrium position, as shown on Fig. 5. As for the interfaces, the interactions between the objects forming the crystal favor a perfectly ordered crystal. The energy of the system can be expanded for small deviations and lead to a quadratic expansion in u characteristic of an elastic energy. It is important to note that for such an expansion to be valid, it is only necessary for the relative displacements $u_i - u_j$ between two neighbors to be small. The displacements themselves can be arbitrary; for example translating the whole crystal by a uniform displacement does not change the energy.

$$H = \frac{1}{2} \sum_{ij} C_{ij} (u_i - u_j)^2, \quad (12)$$

where the C_{ij} are the elastic coefficients of the system. Since the interactions can be long range, the elastic coefficients are not necessarily limited



Disordered Elastic Media, Fig. 4 Measurements of the roughness exponent ζ in two experimental system. These two examples show the algebraic roughness of the domain walls. The top figures are the correlation function (4) of the displacements $B(r)$, and the bottom ones the measured value of the roughness exponent ζ . Left: Magnetic domain walls in thin magnetic films. An exponent of $\zeta \sim 0.6$ is measured compatible with the value $\zeta = 2/3$ expected for a

one dimensional wall in a two dimensional space. [From Lemerle et al. 1998 (Copyright 1998 by the American Physical Society)]. Right: Ferroelectric domain wall in a ferroelectric film. An exponent of $\zeta = 0.26$ is measured. This value is compatible with the value expected for a two dimensional wall in a three dimensional space in the presence of long range dipolar interactions. [From Paruch et al. 2005 (Copyright 2005 by the American Physical Society)]

to nearest neighbor only. Note that for such an expansion to be meaningful, it is necessary for the displacements to be uniquely defined. This assumes that there are no topological defects (dislocations, disclinations) in the crystal. Indeed in the presence of such defects, as shown in Fig. 5 the displacements have two different values when circling around the defect. In order to use the elastic approximation it is thus important to ascertain that topological defects are not generated. I will come back to this crucial point below.

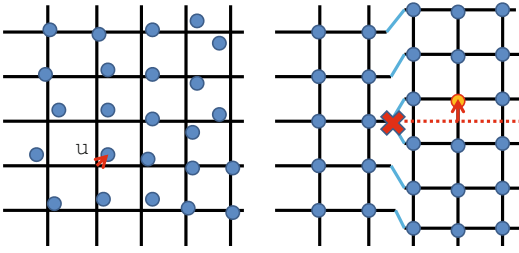
As with the interfaces, the minimum energy configuration is the perfect crystal with all $u_i = 0$. In the absence of disorder this perfect crystal can be affected only by thermal fluctuations. If

temperature becomes too large the crystal will melt. A rule of thumb for melting is when the relative displacements between two neighbors become a sizeable fraction of the lattice spacing

$$\langle (u_i - u_{i+1})^2 \rangle = C_L^2 a^2, \quad (13)$$

where $\langle \dots \rangle$ denotes the thermal average and C_L is a phenomenological constant which turns out to be of the order of $C_L \sim 0.1$ to reproduce reasonable values for the observed melting of solids. This rule of thumb, called the Lindemann criterion for melting, gives, in fact, quite decent results.

In the presence of disorder, one must add to the elastic energy term (12) the energy coming from



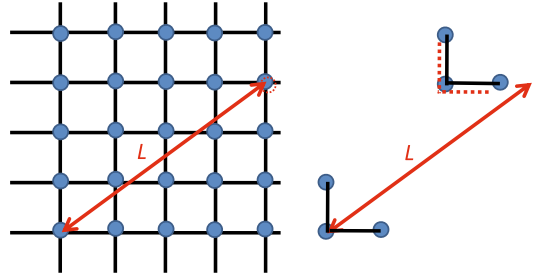
Disordered Elastic Media, Fig. 5 For a periodic system the ability to define a displacement $u(r)$ for the objects (blue dots) compared to the perfect lattice (here a square lattice corresponding to the intersections of the black lines), necessitates the absence of topological defects. Left: if there are no topological defects one can associate, for each site R_i^0 of the perfect lattice, a displacement u_i , as indicated by the red arrow. Right: here there is a topological defect, denoted by the red cross, corresponding to the addition of one line of particles. In this case the displacement u_i is not univalued. From the point of view of the particles on the left of the topological defect, the orange particle has a displacement u of half a lattice spacing, while one could surmise $u = 0$ looking only at particles on the right of the topological defect

the random potential created by the disorder. This takes the form

$$\begin{aligned} H_{\text{dis}} &= \int d^d r V(r) \rho(r) \\ &= \int d^d r V(r) \sum_i \delta(r - R_i^0 - u_i) \end{aligned} \quad (14)$$

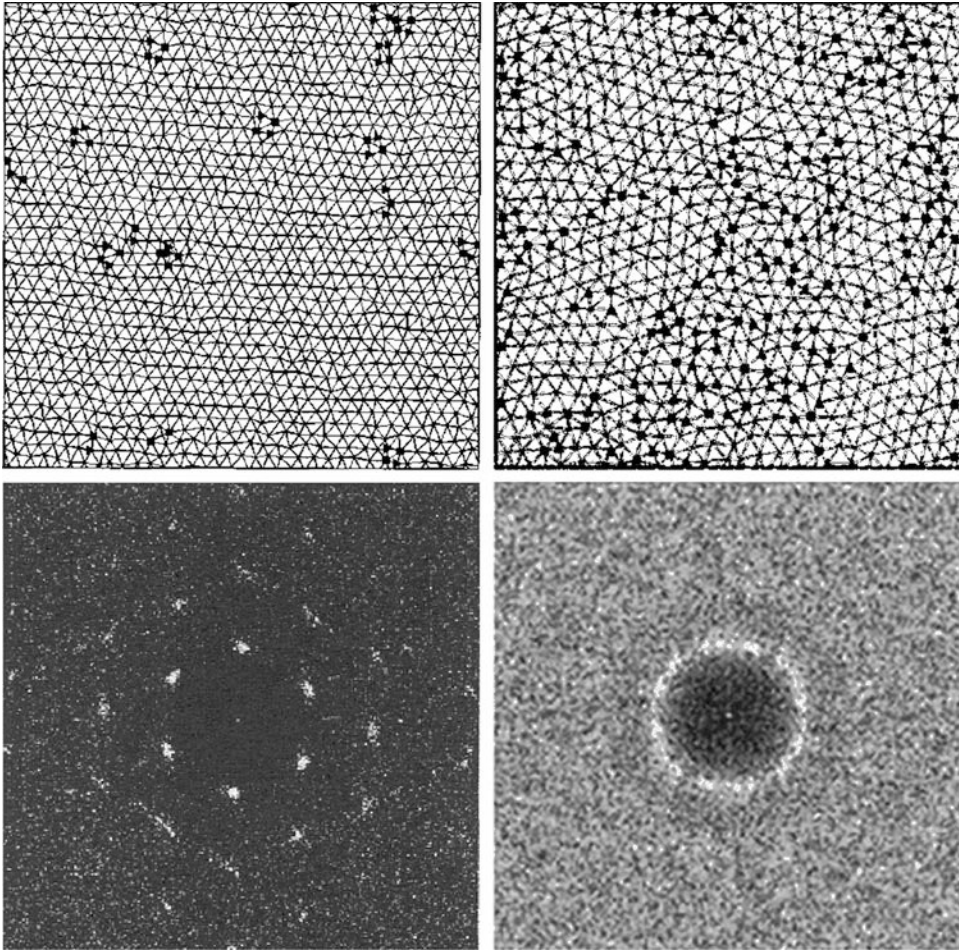
and this term will clearly tend to disorder the crystal.

The case of a periodic system constitutes a specially important and interesting situation. Indeed, the nature of order and the possible phases are more complex than they are for interfaces. An important question is thus whether these two systems are in the same universality class or not. In a general way, the order in a periodic system is characterized by a positional order, indicating that, knowing the position of a reference particle, one can find a particular particle of the solid at a given position. This positional order can be measured by the structure factor, which is the correlation function of the Fourier transform of the density $S(q) = \langle |\rho_q|^2 \rangle$. In a perfect crystal, the structure factor has *divergent* peaks at the position of the reciprocal vectors K_0 of the perfect lattice.



Disordered Elastic Media, Fig. 6 A periodic system possesses positional, orientational and topological order. Left: positional order. A solid has perfect positional order if, by knowing the position of a reference particle, one can predict the position of a particle at distance L as indicated by the dashed circle and the red arrow. Right: orientational order. A solid has orientational order if, by knowing the orientation of the bonds in a region of space, one can predict the orientation at a distance L as indicated by the red dashed lines. Note that the system need not possess positional order for the orientational order to exist. Topological order: topological order exists if, after a triangulation, the topology (i.e., the number of neighbors) of each point of the solid is fixed and the displacements can be defined in a univalued manner. The picture on the left possesses perfect topological order

The presence of such divergent peaks indicates a perfect positional order. The fact that one sees peaks also indicates the existence of another type of order, namely the orientational order in a solid. This is illustrated in Fig. 6. The orientational order indicates that if the bonds have a certain orientation in a region of space, this orientation is preserved in the other parts of the solid. Losing the orientational order replaces the peaks in the structure factor by a ring since the orientation of a given peak is not defined any more. In standard solids, both orders are usually lost at the same time and the solid melts to a liquid, usually by a first order phase transition. But we also know that in some cases for pure systems, such as two dimensional solids, the melting may occur as a two step process where the positional order is lost first and only then the orientational order, leading to a so called hexatic phase (Nelson 1978). A summary of the various cases is shown in Fig. 7. In addition to these standard order parameters, a periodic system is also characterized by a topological order corresponding to the fact that the connectivity of the perfect crystal is preserved by small displacements. Such order is determined



Disordered Elastic Media, Fig. 7 Decoration images of vortex lattices, illustrating the difference between solid and liquid phases. The top figures are the images in real space, while the bottom ones are the structure factor $S(q) = \langle |\rho(q)|^2 \rangle$. Left: the system is in a solid-like phase (in fact a Bragg glass phase (see text)). The system possesses good positional order and orientational order. This can be seen both from the pictures in real space and from the structure factor that shows Bragg peaks at the position of the reciprocal vectors K_0 of the perfect underlying lattice. As shown by the *triangulation*, most sites have six neighbors.

Topological defects where sites have five or seven neighbors (as indicated by the triangles and square marks respectively) do exist, but are paired in 5–7 pairs, making the system free of topological defects at large length scales. Right: the system is in a liquid-like phase. Positional order and orientational order are lost. The Bragg peaks are gone and the structure factor has a ring-like structure (indicating the loss of orientational order). Topological defects are proliferating and are unpaired, contributing to the exponential decay of order in the system. [Images from M. Marchevsky, J. Aarts, P.H. Kes (unpublished)]

by a triangulation of the solid and a determination of the topology. If the topology is identical to that of the perfect lattice, it means that the displacements can be defined in a univalued way across the solid. In the liquid, topological defects such as dislocations and disclinations destroy this perfect topological order and the very concept of displacements around an equilibrium position

becomes ill defined, since in that case the displacement field is no longer univalued.

As for interfaces, disorder changes the properties of the pure elastic system. In order to take into account the effect of disorder on periodic systems, it is thus important to address two different aspects of the problem: a) the effect of the disorder on an approximation of the real system given by elastic

theory; b) whether the disorder is able to generate topological defects, in which case the very idea of an elastic approximation breaks down and another starting point should be found.

As was shown in the groundbreaking paper by Larkin (1970), there always exists for $d \leq 4$, a characteristics length scale L_a for which the displacements become of the order of the lattice spacing a of the perfect crystal. The fact that displacements can become as large as the lattice spacing indicates that *perfect* positional order is lost. The question of *how* this destruction takes place and the nature of the resulting phase is a long standing problem. Given the complexity of the question, no solution existed until recently, but it is interesting to see that the community converged, by inference, on closely related models, to a consensus that was accepted for a long time but eventually proved wrong. The route followed was to learn as much as possible from the interfaces. At short distance, one can make an expansion in powers of the displacements, and the system is described by the Larkin model. This ceases to be valid at the Larkin length L_c , for which the displacements become of the order of the size r_f of the particle in the solid. Note that L_c and L_a are in general two different length scales since the size of the particle r_f and the lattice spacing a are usually different. Naturally, one has $L_c < L_a$. For systems such as the vortex lattice or Wigner crystals, the difference can be huge, while for charge-density waves, one expects to have $r_f \sim a$ and thus $L_c \sim L_a$. Below the Larkin length the system is described by the Larkin model and thus by an algebraic growth of the displacements with a roughness exponent of $\zeta = (4 - d)/2$. Above the Larkin length L_c , but for displacements smaller than a (i.e., for lengths smaller than L_a), one can consider that the various objects of the periodic system don't see each other except by their elastic forces. In particular, they do not sample the same random potential given the smallness of the displacements. One thus has a regime very similar to the random manifold regime of the interface. The displacement continues to grow algebraically, $u \sim L^\zeta$, albeit with a different exponent. Above L_c , the connection between the growth of the displacements and the structure factor (the density

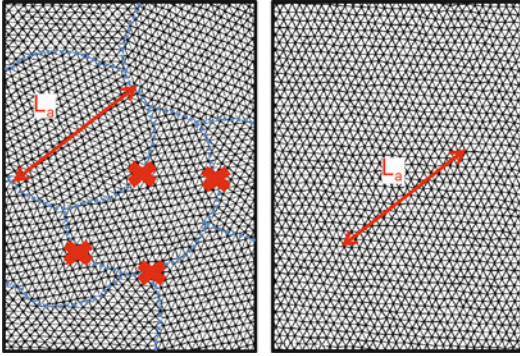
density correlations) is non-trivial since the model is non-Gaussian. Indeed the structure factor is given by (Giamarchi and Le Doussal 1995a).

$$S(K_0 + q) = \int d^d q e^{iqr} C(r), \quad (15)$$

where

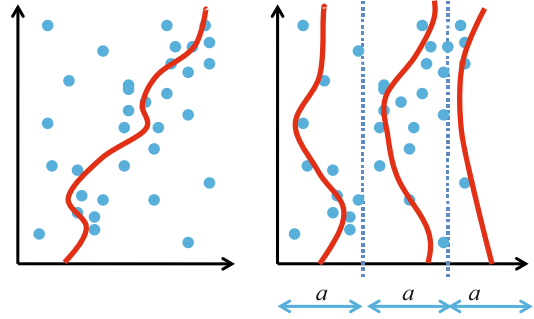
$$C(r) = \left\langle e^{iK_0 u(r)} e^{-iK_0 u(0)} \right\rangle. \quad (16)$$

For Gaussian models such as the Larkin model, one had $C(r) = \exp[-K_0^2/2B(r)] \sim \exp[-K_0^2/2r^{2\zeta}]$ indicating a stretched exponential decay of positional order. Such an exponential decay of positional order would lead to non-divergent peaks in the structure factor. The constant finding of algebraic roughening, and the existence of the length scale L_a seemed to suggest that even beyond L_a the roughening is also algebraic, with perhaps another exponent. One would thus naively expect $C(r) \simeq \exp[-K_0^2/2a^2(r/L_a)^{2\zeta}]$ giving Lorentzian like non-divergent Bragg peaks with a width controlled by $1/L_a$. In addition to this exponential loss of positional order occurring even in the elastic theory, one could question the very starting point of the analysis, namely, the elastic limit and the single-valuedness of the displacements. One could indeed expect topological defects (dislocations, disclinations etc.) to be generated at the scale L_a where the displacements are of the order of the lattice spacing a . Indeed there are arguments (Fisher et al. 1990) (incorrect, as we will see) “showing” that *an arbitrarily small disorder* would always generate topological defects at length scale L_a , leading definitely to an exponential loss of positional order beyond this length. All these elements thus seemed to click together to suggest the picture of a crystal broken into little crystallites of size L_a as shown in Fig. 8. A consensus was thus reached in the community that disordered periodic systems would just lose translational order, and some theories for the vortex lattices were built on this incorrect premise. However this picture crumbled on two



Disordered Elastic Media, Fig. 8 Left: the (incorrect) image of an elastic medium in presence of disorder. The system would be broken into “crystallites” of size L_a characteristic size for which the displacements become of the order of the lattice spacing a ($u(L_a) \sim a$). At the same length scale to release part of the elastic energy due to disorder, the system would prefer to create topological defects (schematically indicated by the red crosses). Beyond the size L_a indicated by the blue dashed line, positional order would be lost exponentially quickly. Right: the Bragg glass, describing the properties of a disordered periodic system in the presence of weak disorder. Although positional order is destroyed at large length scale, and the length scale L_a for which displacements are of order a exists, the system preserves quasi-long range positional order, and perfect topological order. No “crystallite” is thus associated with the length scale L_a , and no topological defects are generated by the disorder

fronts. On the experimental side, it was in direct contradiction with experiments showing, for example, extremely large regions free of defects (Grier et al. 1991; Kim et al. 1996) or a first order melting (Schilling et al. 1996), which was hardly compatible with a very disordered solid in which all positional order would have been lost from the start. On the theory side, our understanding of glassy systems reached a point where better solutions of this problem can be found. The displacements were found to grow in fact only logarithmically (Giamarchi and Le Doussal 1995a; Nattermann 1990; Korshunov 1993; Giamarchi and Le Doussal 1994) with distance $B(r) = A'_d \log(r)$ (or $u(L) \sim \log(L)^{1/2}$). The prefactor A'_d was computed using either a variational approach (Giamarchi and Le Doussal 1995a; Korshunov 1993; Giamarchi and Le Doussal 1994) or an FRG one (Giamarchi and Le Doussal 1994, 1995a). Elastic disordered systems have, therefore, a completely different



Disordered Elastic Media, Fig. 9 Schematic explanation of the difference of roughness between interfaces and periodic systems. Left: In an interface, a high degree of roughness is produced by the fact that there are always regions where it is energetically favorable for the line to go, and from there further to another region, endlessly increasing the displacements. Right: For a periodic system (here a periodic system of lines of period a), since what counts is the *total* energy of the system, there is no interest for one line to make displacements much larger than the interline distance, since it would just steal disorder from the neighbor. Thus, even with the same disorder, displacements would “saturate” (in fact still grow but very slowly with distance) when they reach the inter particle distance

roughness than interface systems. This a priori surprising behavior can be explained in a qualitative way as shown in Fig. 9. Quite interestingly the structure factor and positional order could still be computed for the full model (Giamarchi and Le Doussal 1994, 1995a), and it was shown that in a quite nontrivial way, the relation $C(r) = \exp[-K_0^2/2B(r)]$ remains essentially applicable, leading to a *power-law* decay of positional order $C(r) \propto (1/r)^\eta$, where the exponent η , is for all practical purposes, a number determined only by the dimension (Bogner et al. 2001). For example $\eta = 1-1.2$ for a three dimensional vortex lattice. The algebraic decay of positional order as well as the value of the exponent indicated that the system still retained *divergent* Bragg peaks in its structure factor and thus, although indeed losing positional order, the loss was very slow and the system was nearly as ordered as a perfect solid. Furthermore, it has been shown (Giamarchi and Le Doussal 1995a) that the argument claiming that disorder would always generate dislocations was incorrect and that, on the contrary, due to the slow algebraic decay of the positional order, a three dimensional

system is *stable* to the generation of dislocations, at least when the disorder is below a certain threshold. This has led to a physics for a periodic disordered system radically different from the generally accepted consensus. In particular, consider the two following facts: (a) algebraic (quasi-long range) decay of the positional order, and divergent Bragg peaks; (b) absence of topological defect has led to the prediction (Giamarchi and Le Doussal 1995a) that the disordered periodic system are in fact in a new state of matter, the Bragg glass. Such a system is a disordered system with glassy properties: an energy landscape with many metastable states and the dynamics of a glass, but which “looks” nearly as ordered as a perfect solid. After the Bragg glass was first predicted, its existence has been supported by further analytical (Carpentier et al. 1996; Kierfeld et al. 1997; Fisher 1997) and numerical (Gingras and Huse 1996; Otterlo et al. 1998) calculations.

The existence of the Bragg glass phase has important consequences and makes it possible to reconcile several apparently contradictory results on the phase diagram of the vortices. It allows us to explain that very large regions free of dislocations can be observed (Grier et al. 1991; Kim et al. 1996) while the system is obviously pinned by the disorder. It also explains (Giamarchi and Le Doussal 1995b) the narrow peaks observed in neutron scattering experiments (Yaron et al. 1994; Ling et al. 2001), with a width given by the experimental resolution, which were indicating an excellent degree of positional order. The power-law nature of the peaks has been directly tested in neutron scattering experiments, proving directly the existence of the Bragg glass phase (Klein et al. 2001). In addition to its intrinsic properties, the presence of the Bragg glass phase puts strong constraints on the phase diagram. Indeed, since it is a phase without free topological defects, this phase has to “melt” either when the temperature becomes too high or the disorder too strong, since topological defects have to appear. In vortex systems the latter can be done by changing the magnetic field. The Bragg glass thus provides a very natural explanation (Giamarchi and Le Doussal 1995a, 1997; Ertas and Nelson 1996)

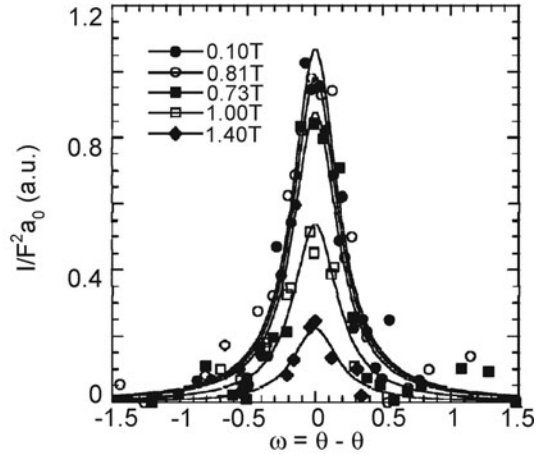
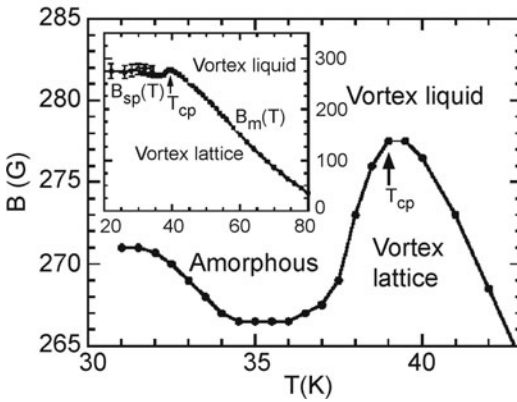
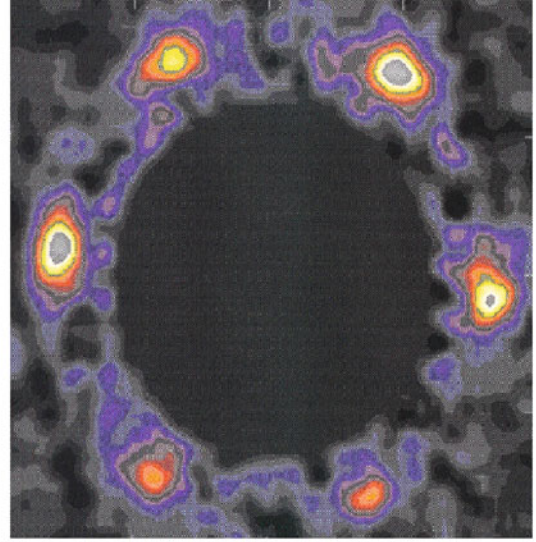
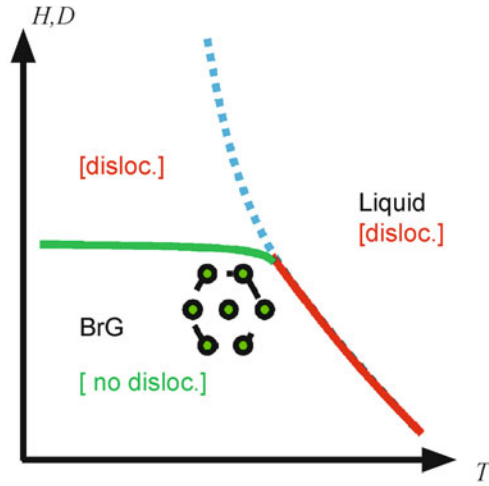
for the existence of a “melting” phase transition as a function of the magnetic field (Khaykovich et al. 1996; Deligiannis et al. 1997), such a transition being associated with the destruction of the Bragg glass phase (Paltiel et al. 2000; Avraham et al. 2001). An example is shown in Fig. 10.

This section can cover only a fraction of the physics of periodic systems, and several other questions have been explored. I refer the reader to the above mentioned literature on the subject for more details.

Pinning and Dynamics

Let us now turn to dynamic properties. One of the main interests of such systems is the fact that their dynamics can easily be probed. Indeed most of these systems can be set in motion by an external force acting directly on the interface or on the crystal, and the velocity v versus force F characteristics are directly measurable. As mentioned before, this is of special importance since these characteristics are linked to paramount properties of the systems (voltage current for vortices, current-voltage for CDW and Wigner crystals, velocity-applied magnetic field for magnetic domain walls). In addition to this practical importance, the dynamics will reflect, even in a more dramatic way than the statics, the competition between disorder and elasticity. In particular, one can expect the dynamics to be dramatically sensitive to the glassy properties and the energy landscape.

The main issues relating to the application of an external force are shown in Fig. 11. In the presence of disorder it is natural to expect that, at zero temperature, the system remains pinned and polarizes only under the action of a small applied force, i.e., it moves until it locks on a local minimum of the tilted energy landscape. At a larger drive, the system follows the force F and acquires a nonzero asymptotic velocity v . So a first set of questions is prompted by the zero temperature properties: what is F_c and how can it be computed? In addition, the $v - F$ curve at $T = 0$ is reminiscent of the curve of an order parameter in a second order phase transition.

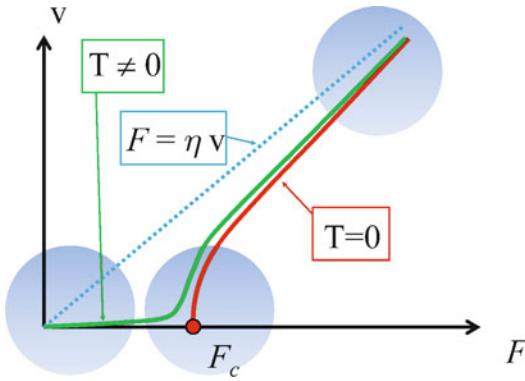


Disordered Elastic Media, Fig. 10 Left top: Schematic theoretical phase diagram for vortices as a function of the temperature T and the magnetic field H , or the disorder D . The Bragg glass (BrG) that has perfect topological order can melt either due to thermal fluctuations (red line) or because the disorder becomes too large (green line). The existence of the Bragg glass thus implies a single melting curve having a crossover between these two regimes. The melting of the Bragg glass thus explain the existence of a transition as a function of the magnetic field. The blue dashed line would be the melting line of the solid in the absence of disorder (After Giamarchi and Le Doussal 1997). Left bottom: Measured phase diagram for high temperature superconductor BSCCO, showing that both

melting transitions with temperature and with magnetic field are indeed the same melting curve. [From Avraham et al. 2001 (Copyright 2001 by the Nature group)]. Right: Neutron diffraction on the superconductor BKBO. The structure factor shows clear Bragg peaks, indicating the good degree of both positional and orientational order despite the disorder present in the sample. As shown in the bottom diagram the width of the structure factor does not change when the magnetic field is changed, since it is controlled by the experimental resolution, while the height decreases. This is in agreement with the consequences of a power law divergent Bragg peak, and is thus a test of the existence of the Bragg glass. [From Klein et al. 2001 (Copyright 2001 by the Nature group)]

Here, the system being out of equilibrium, no direct analogy is possible, but this suggests that one could expect $v \sim (F - F_c)^\beta$ with a dynamical critical exponent β . Whether such an

analogy to critical phenomena holds and what the physical consequences and calculation of such exponents might be are, of course, important questions.



Disordered Elastic Media, Fig. 11 The velocity v induced by an external force F of a disordered elastic system. In the absence of pinning and with a damping coefficient η the steady state velocity $v = F/\eta$ is reached. At zero temperature $T = 0$ the system stays pinned until a critical force F_c is reached. At finite temperature a motion can occur even for forces below the threshold $F < F_c$, since the barriers to motion can always be passed by thermal activation. One can distinguish three very different regimes in this curve: large velocity, depinning and small force response (creep)

Another important set of questions pertains to the nature of the moving phase itself, and in particular to behavior at large velocity: to what extent does this moving system resemble the static one? This concerns both the positional order properties and the fluctuations in velocity such as the ones measured in noise experiments. Can we expect novel physics there, or is the system simply “surfing” over the disorder?

Finally, how does the system respond to a very small applied force? We are accustomed to the fact that a normal system when perturbed usually responds linearly to the perturbation. We could thus naively expect $v \propto F$, with a coefficient that would define the “mobility” of the interface. Is this true, or, due to the glassy nature of the system, do we have nonlinear response and more complicated physics?

General Description of the Dynamics

Computing the dynamics is not an easy task. Let me illustrate the method using the case of the interfaces. The displacement field in each point is now a function of the time $u(r, t)$ and has to obey the equation of motion. The starting point is the equation of motion

$$m \frac{d^2 u(r, t)}{dt^2} + \eta \frac{du(r, t)}{dt} = \sum F, \quad (17)$$

where η is a friction coefficient that phenomenologically describes the dissipation processes that take place inside the object (interface, etc.) when there is motion. Usually one is interested in the steady state motion of the system, in which case in the long time limit, the second order derivative becomes smaller than the first order one and a good approximation is to take $m = 0$ in the above equation.

The forces are of two types. There are the forces deriving from a Hamiltonian

$$F[u(r, t)] = - \frac{\partial H[u]}{\partial u(r, t)}. \quad (18)$$

The two main contributions (elastic and disorder) lead in the equation of motion to the elastic forces trying to keep the interface flat, and to the pinning forces. In addition to these forces that would be present in equilibrium, one must add two other forces: The first one is the external force. I consider here only the simple case of a constant external force F . In the presence of this force and in the absence of pinning it is natural to expect the system to reach a steady state velocity $v = F/\eta$. Note that such a state, although time-independent, cannot be described by an equilibrium theory. In particular, the fluctuation dissipation theorem, relating in equilibrium the fluctuations in the absence of a perturbation and the response of the system to an external perturbation, is not in general obeyed any more. The second force is needed if we want to describe the system at a finite temperature. In that case, one must add (Zinn-Justin 1989) a Langevin force $\zeta(z, t)$ which is a noise with correlations

$$\langle \zeta(r, t) \zeta(r', t') \rangle = \eta T \delta(r - r') \delta(t - t'). \quad (19)$$

The equation of motion thus becomes, in its simplest incarnation,

$$\eta \frac{du(r, t)}{dt} = - \frac{\partial H[u]}{\partial u(r, t)} + F + \zeta(r, t). \quad (20)$$

As is well known, the presence of Langevin noise ensures that, in the absence of an external

force F , the time evolution of the system reproduces the thermodynamic ensemble average. In other words, the equal time correlations $\langle u(z, t) u(z', t) \rangle$ obtained by averaging over the thermal noises, are identical to the equilibrium correlation function $\langle u(z) u(z') \rangle_H$ that one would have obtained for a system with the Hamiltonian H at the temperature T .

In the absence of disorder the equation becomes quite simple and is known as the Edwards–Wilkinson equation

$$\eta \frac{du(r, t)}{dt} = -\nabla_r^2 u(r, t) + F + \zeta(r, t). \quad (21)$$

The system thus slides at a constant velocity $v = F/\eta$ and one can see that in the moving frame the interface is at equilibrium, since the change of variable $u(r, t) = \frac{F}{\eta}t + \delta u(r, t)$ gives for the relative displacements $\delta u(r, t)$ exactly the same equation as in equilibrium in the absence of any external force. Even in this simple case, there are several effects of the motion that need to be taken into account, in particular the presence of a cutoff in the system generates terms that would not normally have been incorporated in the original equation of motion and that can modify the behavior of the system. The most well known is the so called Kardar–Parisi–Zhang (KPZ) term (Kardar et al. 1986).

In the presence of disorder, the equation of motion becomes extremely complicated to solve since the pinning force is a random variable depending on the particular realization of the disorder, and a double averaging must be done, both on the thermal noise and on the disorder. No perfect method exists to treat such an equation. Since we are usually better equipped to deal with integrals than with differential equations, especially with stochastic terms, a convenient rewriting of this equation exists, which formally gives back the equivalent of a path integral and an action. This is the so-called Martin–Siggia–Rose (MSR) formalism (Janssen 1976; Martin et al. 1973). I refer the reader to the literature on this relatively specialized method (Zinn-Justin 1989). The advantage is that it allows averaging over the disorder from the start. This

in particular paves the way for an FRG treatment of the problem.

Depinning

The first set of questions arises around depinning. Indeed, in the presence of disorder the naive expectation is that the interface is unable to move, at zero temperature, below a certain threshold of force F_c called the pinning force. Computing this pinning force is not easy. In a remarkable feat of physical intuition, Larkin has shown that the pinning force can be directly obtained from the static behavior of the system (Larkin and Ovchinnikov 1979). Indeed, the idea is that the pinning force is related to the appearance of many metastable states and the presence of random potential. Because it is quadratic in the displacements, the Larkin model does not exhibit a pinning force. The idea would thus be to relate the pinning force to the length scale at which the Larkin model ceases to pertain. As we discussed before, this is the length L_c for which the displacements are of the order of the correlation length of the random potential or the width of the elastic object. At that scale, the elastic plus disorder energy scales as $cL_c^{d-2}r_f^2$ while the additional energy due to the force scales as

$$H_F = \int d^d r F u(r) \sim F L_c^d r_f. \quad (22)$$

Balancing the two terms leads to the famous Larkin collective pinning force

$$F_c = \frac{c r_f}{L_c^2}. \quad (23)$$

This is a remarkable relation since it relates a dynamic property to purely static quantities. This intuitive result can be substantiated by considerably more complicated calculations. In the next section we will see another rough estimate based on a large velocity expansion. Finally, starting from the equation of motion (17), it is possible to obtain F_c from an FRG calculation (Nattermann et al. 1992; Chauve et al. 2000), confirming, from this microscopic calculation, Larkin’s result. Numerical methods have allowed an extremely

precise calculation of F_c (Rosso and Krauth 2002b).

Besides the existence of the pinning force itself, the description of depinning is a considerable challenge. A very fruitful line of approach for this problem was suggested by D.S. Fisher (1985). Indeed, looking at the $v - F$ characteristics is strongly reminiscent of the curve of an order parameter as a function of temperature in a second order phase transition (zero for $T > T_c$ and non-zero for $T < T_c$). This strongly suggests using an analogy with a standard critical phenomenon to analyze the depinning. In particular, one can infer from this analogy that a divergent length scale exists at the transition, and that one can define scaling behavior and critical exponents as a function of this length scale. One can define a critical exponent for the velocity $v \sim (F - F_c)^\beta$, for the correlation length $\xi \sim (F - F_c)^{-\nu}$ and a dynamical exponent relating space and time divergences $\tau \sim \xi^z$. These exponents are related by scaling relations, analogous to those of standard critical phenomena and that can be computed by looking at the scaling of the equation of motion. The scaling relations are

$$v = \frac{\beta}{2 - \zeta} = \frac{1}{z - \zeta}. \quad (24)$$

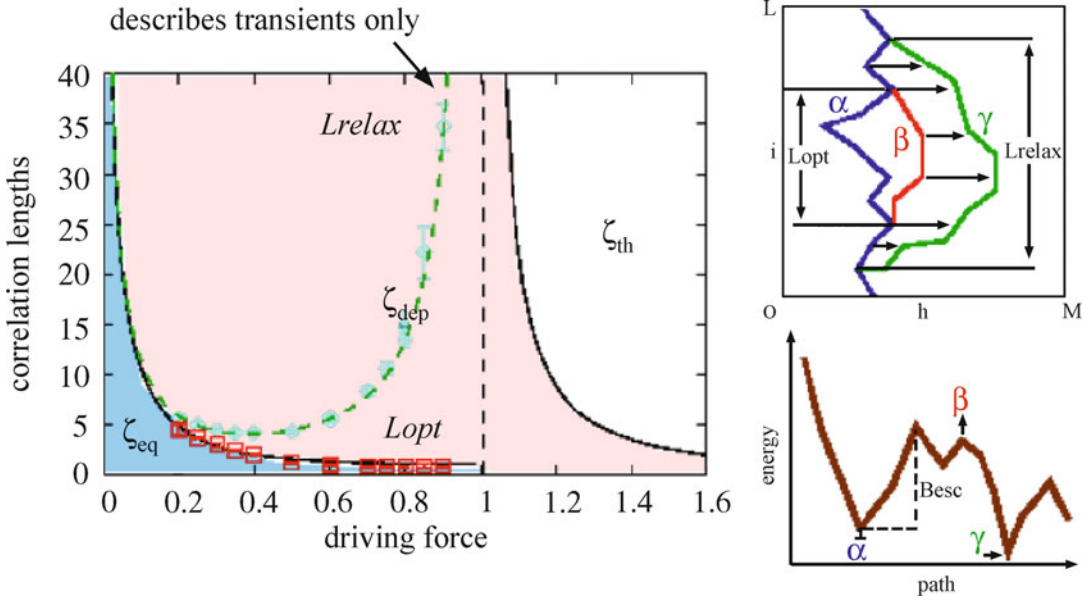
Such scaling behavior is directly confirmed from solutions of the equation of motion, either from FRG or from numerical simulations. The length scale ξ can be identified as the length scale of avalanches. Computing and measuring these exponents is a considerable challenge and sophisticated FRG (Le Doussal et al. 2004; Nattermann et al. 1992; Chauve et al. 2000; Narayan and Fisher 1993) or numerical (Rosso and Krauth 2002b; Duemmer and Krauth 2005) techniques have been developed for this goal.

In addition to these quantities characterizing the motion of the line, other important physical observables are modified by the application of external force. This is in particular the case of the roughness of the line. Right at depinning $F = F_c$, the line is much more rough than when in equilibrium, since it is on the verge of depinning. There is thus a new roughness exponent ζ_{dep} which can be computed and is $\zeta_{\text{dep}} \sim 1.2$ for a one dimensional interface.

This result has two very important consequences. The first one comes from the value of the roughness exponent itself. Since, at least for a line, this value is larger than one, this immediately suggests that close to depinning the elastic model will run into trouble. Indeed when u scales more than linearly with distance, the very basis of the elastic approximation $\nabla u \ll 1$ is violated at large length scales. The line will thus have to generate defects (overhangs) to heal this fact. The nature of the resulting physics when this is taken into account is a challenging and yet open question. The second observation concerns the steady state aspect of the line. At large length scales, because of finite velocity, the system will average over the disorder. We will come back in more detail to this point in the next section, but for the moment, stick with this simple vision. In this case, beyond the length ξ one can expect the disorder to be irrelevant and thus to recover the pure thermal roughness exponent. The system will thus have the depinning roughness exponent ζ_{dep} for length scales below ξ and the thermal one ζ_{th} for length scales above ξ . This is summarized in Fig. 12. One important question now is what happens at a small but finite temperature. The first effect is, of course, to smooth the $v - F$ characteristics. This leads to the important question of whether one can define a scaling with the temperature of this thermal rounding of the depinning (see e.g., Bustingorry et al. 2008 and references therein). Even more interesting is the question of the roughness of the line. The analogy with a critical phenomenon would simply suggest that a similar divergent length scale should exist for $F < F_c$, leading to the standard pattern of “critical regime”. However, as indicated in Fig. 12, such a divergent length scale does not exist (Kolton et al. 2006). This leads to a very puzzling behavior and shows that although the analogy with standard critical phenomena can be extremely fruitful, it must be taken with a grain of salt. The depinning, which is by essence a dynamical transition, possesses its own physics.

High Velocity Phase

Another important set of questions and physics occurs when the interface is moving at large velocity, i.e., for $F \gg F_c$. This is apparently the



Disordered Elastic Media, Fig. 12 Close to depinning the motion proceeds by avalanches between two configurations α and γ . Above F_c , there exists a divergent length scale (L_{opt} on the figure) below which the line is characterized by the roughness exponent ζ_{dep} and above which the line shows the thermal roughness ζ_{th} . A normal critical phenomenon would have had a similar divergent length scale for $F < F_c$. This is not the case for the depinning. A transient divergent length scale L_{relax} does exist, but does

not show up in the steady state properties of the line. Contrary to naive expectations from a “standard” critical phenomenon, one observes the equilibrium roughness exponent ζ_{eq} at *short* distances. This shows that the analogy between depinning and “standard” critical phenomena, although very fruitful, must be taken with a grain of salt. On the right, the schematic shape of the line and energy profiles are shown. (After Kolton et al. 2006)

simplest regime since one could expect that at large velocity one has a control parameter on the theory and that an expansion in $1/v$ is possible. This is indeed the case for the $v - F$ characteristics. A large velocity expansion of the disorder term can be made by going into the moving frame of the elastic media. One can indeed write $u(r, t) = vt + \delta u(r, t)$, where $\delta u(r, t)$ describes the displacements in the moving frame. Because the system surfs over the disorder at very large velocity one can expect the effects of the disorder, and hence $\delta u(r, t)$, to be small. This is confirmed by a well controlled large velocity expansion (Larkin and Ovchinnikov 1974; Schmidt and Hauger 1973). In particular, the correction due to the disorder to the velocity can be computed and behaves as

$$\frac{F - \eta v}{\eta v} \propto D \left(\frac{1}{\eta v} \right)^{\frac{4-d}{2}}. \quad (25)$$

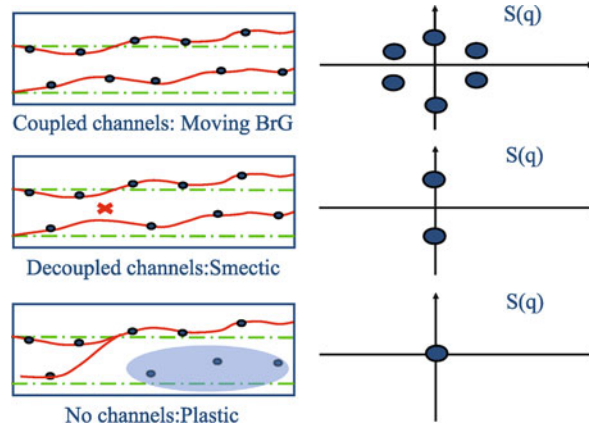
This shows clearly that the effects of disorder are kept small at large velocity or large force and become increasingly important as the force/velocity gets smaller, in agreement with Fig. 11. The relative correction to the velocity grows in dimensions smaller than $d = 4$, confirming that disorder is relevant below this dimension. Although one cannot extrapolate the perturbative expressions, a crude way to estimate the critical force F_c is when the deviations (25) become of order one. This method gives back the estimate (23) for F_c , obtained from totally different considerations.

The large velocity expansion also allows us to address the physics of the moving phase, namely the shape and properties of the elastic system in the moving frame. A calculation of these effects was performed (Koshelev and Vinokur 1994) by computing the displacements δu from the large velocity expansion. This leads to the striking result that at large velocity the effect of disorder

disappears and can be absorbed in a simple modification of the temperature of the system, leading to an effective temperature T_{eff} . This has important consequences on the properties of the system in the moving frame. For an interface, this is consistent with the idea, exposed in the previous section, that at large distance one recovers the thermal roughening exponent. For periodic systems, since there is the possibility of melting, this has the more drastic consequences that driving the system could induce a velocity controlled melting. Indeed, for large velocities, the effective temperature is small, while for smaller velocities it would be large. The system would thus be a disordered system while static, then close to depinning, where the effective temperature would be large, it would be in a melted (liquid) state, and would then recrystallize when moving at larger velocities.

Although the concept of effective temperature is extremely fruitful, in particular for this dynamic recrystallization, the properties of the moving periodic system are richer (Giamarchi and Le Doussal 1996) than those of a simple solid subjected to temperature. Indeed, periodic systems have a

structure in the direction *transverse* to the direction of motion. This structure, and the corresponding disorder structure, cannot be averaged by the motion, however large the velocity remains. This leads to the fact that disorder remains even when the system is in motion. In other words, a moving periodic system remains a glass. The way the motion takes place is quite peculiar. The system finds optimal paths (Giamarchi and Le Doussal 1996) which are a compromise between the elastic energy, disorder and the motion. These paths are rough, similar to the way in which a static system in a disordered environment is rough. This is shown in Fig. 13. For periodic systems, pinning effects still manifest themselves in the moving system. The glassy nature and the channel motion has been confirmed both numerically (Moon et al. 1997; Kolton and Grønbech-Jensen 1999; Fangohr et al. 2001) and experimentally (Pardo et al. 1998). The channel motion leads to an interesting consequence. Since the effects of disorder are weakening as velocity increases, the channels undergo a transition between a regime for which the particles in different channels are coupled or decoupled (Balents et al. 1998; Le Doussal and Giamarchi



Disordered Elastic Media, Fig. 13 Motion of a periodic system. The system develops rough channels which compromise between elastic energy and the transverse component of the disorder that are poorly averaged by the motion. All the particles follow on these channels like cars on highways. Depending on the velocity, the channels are increasingly coupled: Bottom image: close to depinning, motion can proceed through a plastic regime where unpinned and pinned regions (denoted by the blue circle)

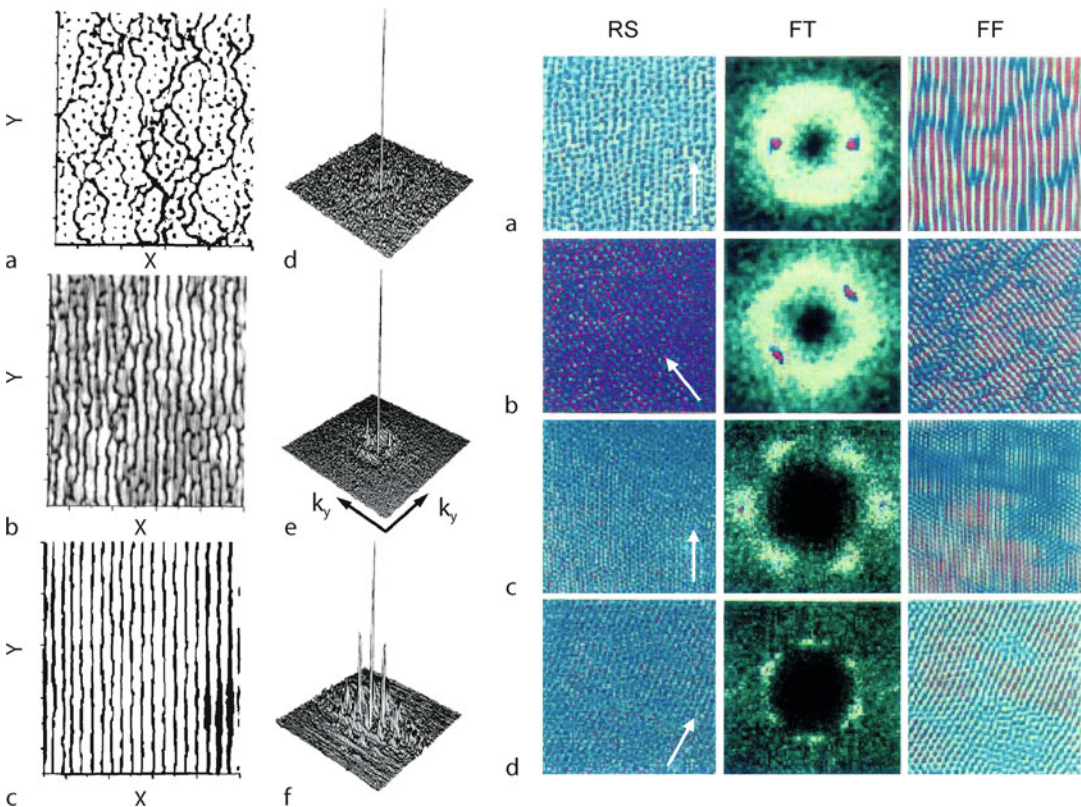
coexist; Middle image: topological defects can exist between the channels, so although the channels themselves are well formed, the particles in them are essentially decoupled leading to a smectic like behavior; Top image: the channels are coupled and the system is a moving Bragg glass with effects of both disorder and elasticity and no topological defects. On the right, the corresponding structure factors are indicated

1998). In the first case, the system is essentially moving as a “solid” (in fact a moving Bragg glass) since the topological order is perfect even if the system is still distorted by disorder. In the second case, the channels are decoupled, which means that a smectic like structure of the particles inside the channels is expected. These transitions as described in Fig. 13 have also been observed both numerically and experimentally as shown in Fig. 14. An additional consequence of the existence of such channels is the existence of a *transverse* pinning force (Giamarchi and Le Doussal 1996; Le Doussal and Giamarchi 1998). Indeed, even if the particles themselves are moving along the channels, the channels themselves are pinned if

one applies an additional force transverse to the direction of motion. This surprising phenomenon has been numerically confirmed (Moon et al. 1997; Kolton and Grønbech-Jensen 1999; Fangohr et al. 2001), but observing it in classical periodic systems is still an experimental challenge. Experiments showing the absence of Hall effect in Wigner crystal systems (Perruchot et al. 2000) could constitute an experimental proof of such a transverse critical force, but clearly further experimental data would be needed to unambiguously decide on that point.

Small Applied Force and Creep Motion

Finally, let us look at the response of the system to a small external force. At zero temperature,



Disordered Elastic Media, Fig. 14 Left: numerical simulations confirming the presence of channels for moving periodic structures and the sequence of transitions depicted in Fig. 13. The left part of the image shows the real space trajectories, while the right part is the structure factor. The force is increasing from the *top* to the *bottom* of the image. [From (Kolton and Grønbech-Jensen 1999) (Copyright 1999 by the American Physical Society)]. Right:

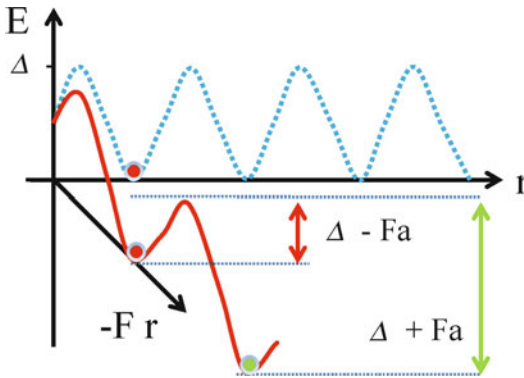
A decoration image of moving vortices also showing the presence of channels. The direction of the applied force is indicated by an arrow. The left column is the raw decoration image, the center one is the Fourier transform giving the structure factor, the right column is a filtered version of the image showing the channels more clearly. [From (Pardo et al. 1998) (Copyright 1999 by the Nature group)]

one is below the pinning force, and thus except for a transient motion the system remains pinned. Motion can thus only take place due to thermal activation over the energy barriers. The response to a small external force is thus a method of choice to probe for the nature of the energy landscape of such systems. For usual systems one expects the response to be linear. Indeed, earlier theories of such motion have found a linear response. The idea is to consider that a blob of pinned material has to move in an energy landscape with characteristic barriers Δ as shown in Fig. 15. The external force F tilts the energy landscape, thus making forward motion possible. The barriers are overcome by thermal activation (Anderson and Kim 1964) (hence the name: Thermally Assisted).

Flux Flow (TAFF)) with an Arrhenius law. If the minima are separated by a distance a the velocity is

$$v \propto e^{-\beta(\Delta - Fa/2)} - e^{-\beta(\Delta + Fa/2)} \simeq e^{-\beta\Delta} F. \quad (26)$$

The response is thus linear, but exponentially small.



Disordered Elastic Media, Fig. 15 In thermally assisted flux flow (Anderson and Kim 1964) a region of pinned material is considered as a particle moving in an energy landscape characterized by characteristic barriers Δ , schematized by the blue dashed periodic potential, of period a . Applying an external force tilts the energy landscape. The motion over barriers can always proceed by thermal activation. Due to tilt, the barrier to forward motion (in red) is smaller than the reverse barrier (in green). This results in an exponentially small but linear response when a small external force is applied to the system

However this argument is grossly inadequate for a glassy system. The reason is easy to understand if one remembers that the static system is in a glassy state. In such a state a characteristic barrier Δ does not exist, since barriers are expected to diverge as one gets closer to the ground state of the system. The TAFF formula is thus valid in systems where the glassy aspect is somehow eliminated and the barriers saturate. This could be the case, for example, for a finite size interface. When the glassy nature of the system persists up to arbitrarily large length scales, the theory should be accommodated to take into account divergent barriers. This can be done qualitatively within the framework of the elastic description using scaling arguments (Nattermann 1990; Ioffe and Vinokur 1987; Nattermann 1987; Feigelman et al. 1989). The basic idea rests on two quite strong but reasonable assumptions: (i) the motion is so slow that one can consider, at each stage, that the interface is motionless and use its *static* description; (ii) the scaling for barriers, which is quite difficult to determine, is the same as the scaling of the minimum of energy (metastable states) that can be extracted, again, from the static calculation. If the displacements scale as $u \sim L^\zeta$ then the energy of the metastable states (see (2)) scales as given by (5): $E(L) \sim L^{d-2+2\zeta}$. Since the motion is very slow, the effect of the external force is simply to tilt the energy landscape

$$E(L) - F \int d^d r u(r) \sim L^{d-2+2\zeta} - FL^{d+\zeta}. \quad (27)$$

Thus, in order to make the motion to the next metastable state, one needs to move a piece of the pinned system of size

$$L_{\text{opt}} \sim \left(\frac{1}{F} \right)^{\frac{1}{2-\zeta}}. \quad (28)$$

The size of the optimal nucleus able to move thus grows as the force decreases. Since the barriers to overcome grow with the size of the object, the minimum barrier to overcome (*assuming* that the scaling of the barriers is *also* given by (5))

$$U_b(F) \sim \left(\frac{1}{F}\right)^{\frac{d-2+2\zeta}{2-\zeta}} \quad (29)$$

leading to the creep formula for the velocity

$$v \propto \exp \left[-\beta U_c \left(\frac{F_c}{F} \right)^\mu \right], \quad (30)$$

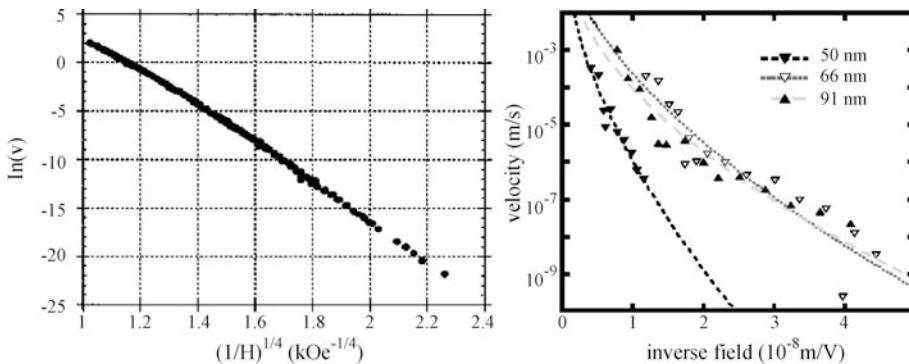
where F_c is the depinning force and U_c a characteristic energy scale and the *creep exponent* μ is given by,

$$\mu = \frac{d-2+2\zeta}{2-\zeta}. \quad (31)$$

Equations (30) and (31) are quite remarkable. They relate a dynamical property to *static* exponents, and show clearly the glassy nature of the system. The corresponding motion has been called creep since it is a sub-linear response. It is a direct consequence of the divergent barriers in the pinned system.

Of course the derivation above is phenomenological, so it is important to ascertain by more microscopic methods whether the results hold. Although in principle one simply has to solve the equation of motion (20), in practice this is quite complicated. A natural framework for

computing perturbation theory in off-equilibrium systems is the MSR formalism. Using this formalism and an FRG analysis, one can confirm the creep formula for velocity (Chauve et al. 2000; Chauve et al. 1998). Numerical simulations also show the absence of linear response and the existence of a creep response (Kolton et al. 2005a). Creep has also been checked experimentally in various systems. Vortices show a creep behavior with an exponent $\mu = 1/2$ compatible with the existence of the Bragg glass ($d = 3$, $\zeta = 0$) (Fuchs et al. 1998). However, the range of measurable velocities makes it difficult to unambiguously check for this law. One spectacular determination of the creep law was performed in a magnetic film (Lemerle et al. 1998). In such a situation the roughness exponent is known exactly ($\zeta = 2/3$) and thus the value of the creep exponent $\mu = 1/4$ is not an adjustable parameter, making it a much more stringent test. As shown in Fig. 16, the velocity was measured over ten orders of magnitude, a spectacular feat, and a remarkable confirmation of the creep law. Measurements of the creep law have also been performed for domain walls in ferroelectrics where a simultaneous measurement of the creep exponent and of the roughness exponent was performed (Tybell et al. 2002; Paruch et al. 2005). As shown in



Disordered Elastic Media, Fig. 16 Experimental verification of the creep law for magnetic and ferroelectric domain walls. Left: Magnetic domain walls. The film is extremely thin, thus the domain is a line in a two dimensional plane, leading to a creep exponent of $\mu = 1/4$. The creep law is observed on about ten orders of magnitude for the velocity. [From Lemerle et al. 1998 (Copyright 1998 by the American Physical Society)]. Right: Ferroelectric

films. A creep behavior is observed over several orders of magnitude giving a creep exponent of $\mu \sim 0.58$. This value together with the measured roughness exponent $\zeta = 0.26$ leads to an effective dimension of $d = 2.5$, well in agreement with a two dimensional domain wall in presence of dipolar forces. [From Paruch et al. 2005 (Copyright 2005 by the American Physical Society)]

Fig. 16 the stretched exponential behavior for the velocity is well verified, and the formula (31) consistent with what is expected for a two dimensional domain wall in the presence of dipolar forces, corresponding to the experimental situation.

The FRG derivation allows us to more deeply probe the physical understanding of the system. In particular it unravels a new phenomenon. Although the velocity itself is dominated by events occurring at the thermal length scale (28), interesting physics takes place beyond this length scale. Indeed, when a portion L_{opt} of the line has been able to move forward by thermal activation over the barriers, it serves as a nucleation center to trigger an avalanche (Chauve et al. 2000) over a much larger length scale L_{av} . The behavior between these two length scales is thus very similar to a depinning phenomenon where temperature plays no role. Although the velocity is dominated by the first process, which is the slow one, the shape of the line reflects this much larger avalanche scale in a way which is compatible with experiments (Repain et al. 2004). The creep, being controlled by the time to overcome divergent barriers in the system, has several other consequences, in particular on the issue of the out-of-equilibrium physics of such systems (Kolton et al. 2005b) and its connection to the aging of glasses (Cugliandolo et al. 1998).

Future Directions

Both because of experimental drive (no pun intended) but also because of theoretical advances and the development of the proper tools, this field has known several breakthroughs in the last decade or so. There is now a good understanding of static properties for both interfaces and for periodic systems, and most of the misconceptions and folklore have been replaced by solid results. Novel phases have emerged such as the Bragg glass phase. Steady state dynamics has also made significant progress, with the understanding of processes such as creep motion. From the point of view of methods, these systems have made it possible to perfect methods to deal with glassy

systems such as replica methods, functional renormalization group as well as special numerical methods. These results have found and continue to find applications in a large variety of experimental domains. Despite these advances, it is clear that many questions remain pending, making it still a very challenging field which is yet in constant progress. Experiments regularly provide new systems and new challenges and stimulate theoretical analysis. Several lines of research are actually open and should carry the bulk of the research in that domain in the future.

From the point of view of the static, although the situation without defects is under control, we know next to nothing when elasticity, disorder and defects are included. For interfaces this means treating the overhangs and bubbles, and for periodic systems all the topological defects such as the dislocations. Although we know now that the situation without defects is robust below a certain threshold of disorder, it is clear that the ability to deal with the strong disorder situation is needed for many experimental systems. This is the case for the high field phase of vortices and strong disorder in the interfaces, both of which are dominated by defects.

In the dynamics, one of the very challenging questions that one has to face is the one of the out-of-equilibrium dynamics, when the system has not yet reached a steady state. A simple example of such a situation would be an interface relaxing slowly from a flat configuration or quenched at low temperatures from a high temperature configuration. Given that these systems are glasses, the time evolution of such cases is highly non-trivial, and should show a generic phenomenon of glasses known as aging. This is directly a situation relevant to many experiments. From the conceptual point of view this is an extremely challenging question since most of the theoretical tools that we have fail to tackle such situations, and thus new tools or new concepts need to be invented.

Last but not least, we have dealt mainly with classical systems here. But disordered elastic systems can also be realized in the quantum worlds as briefly mentioned in the introduction. The question on how to extend the concepts of glasses to quantum systems remains largely open. In

particular, one can expect the dynamics to be affected. Indeed, classical systems can pass barriers only by thermal activation, while quantum systems are good at tunneling through barriers. The extension of the above concepts to the quantum world is thus a very challenging direction.

The gold mine of disordered elastic media is thus far from being exhausted. It seems that each nugget we find is only the opening of a new vein with even richer stones. The variety of experimental realization is ever growing, as is the depth of the questions that are now within our grasp.

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Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems

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Article Outline

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Glossary

Critical point A (phase transition) point in the parameter space of a physical system where the length-scale characteristic of its structure, called the correlation length ξ , becomes infinite and the system displays power law scaling behavior on all available scales. The associated critical power law exponents are universal, i.e., they are independent of the microscopic details of the system.

Earthquake quantities The most common form of earthquake data consists of seismic catalogs that list the time, location, and size of earthquakes in a given space-time domain. The size of earthquakes is usually specified by magnitudes associated with spectral amplitudes of seismograms at a given frequency and site-instrument conditions. The seismic potency and moment provide better physical

characterizations for the overall size of earthquakes. Additional important quantities are the geometry of faulting (e.g., strike slip), stress drop at the source region, and radiated seismic energy.

Mean field theory A theoretical approximation with an interaction field that has constant strength and infinite range. In mean field approximation, every domain interacts equally strongly with every other domain, regardless of their relative distance.

Renormalization group (RG) A set of mathematical tools and concepts used to describe the change of physics with the observation scale. Renormalization group techniques can be used to identify critical points of a system as fixed points under a coarse graining transformation and to calculate the associated critical power law exponents and the relevant tuning parameters. They can also be used to determine what changes to the system will leave the scaling exponents unchanged and thus to establish the extent of the associated universality class of the critical point.

Seismic moment A physical measure of earthquakes given by the rigidity at the source region times the seismic potency.

Seismic potency A physical measure for the size of earthquakes given by the integral of slip over the rupture area during a seismic event.

Strike-slip fault A style of faulting involving pure horizontal tangential motion, predicted for situations where the maximum and minimum principal stresses are both horizontal. Prominent examples include the San Andreas Fault in California, the Dead Sea Transform in the Levant, and the North Anatolian Fault in Turkey.

Tuning parameters Parameters such as disorder, temperature, pressure, driving force, etc., that span phase diagrams. Critical values of the tuning parameters describe critical points of the phase diagrams.

Universality Power law scaling exponents and scaling functions near a critical point are the

same for a class of systems, referred to as universality class, independent of the microscopic details. Universal aspects typically depend only on a few basic physical attributes, such as symmetries, range of interactions, dimensions, and dynamics.

Definition of the Subject

Observations indicate that earthquakes and avalanches in magnetic systems (Barkhausen noise) exhibit broad regimes of power law size distributions and related scale-invariant quantities. We review results of simple models for earthquakes in heterogeneous fault zones and avalanches in magnets that belong to the same universality class and hence have many similarities. The studies highlight the roles of tuning parameters, associated with dynamic effects and property disorder, and the existence of several general dynamic regimes. The models suggest that changes in the values of the tuning parameters can modify the frequency size event statistics from a broad power law regime to a distribution of small events combined with characteristic system-size events (characteristic distribution). In a certain parameter range, the earthquake model exhibits mode switching between both distributions. The properties of individual events undergo corresponding changes in different dynamic regimes. Universal scaling functions for the temporal evolution of individual events provide similar predictions for the earthquake and magnet systems. The theoretical results are generally in good agreement with observations. Additional developments may lead to improved understanding of the dynamics of earthquakes, avalanches in magnets, and the jerky response to slow driving in other systems.

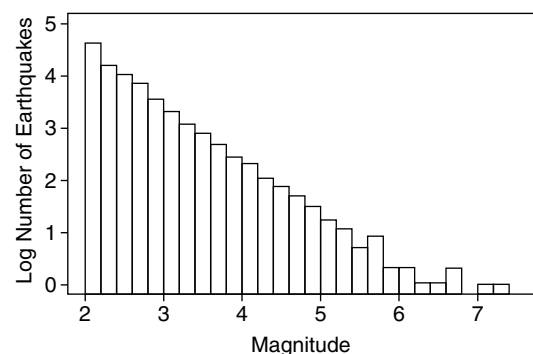
Introduction

Global Statistics and Power Law Scaling

Earthquakes occur in a broad spectrum of sizes, ranging from unnoticeable tremors to catastrophic events. While short-term earthquake prediction is still beyond reach, understanding the statistics of

earthquakes might facilitate longer-term prediction of large earthquakes and statistical estimates of seismic hazard. Gutenberg and Richter (1954) found that the frequency of observed regional and global earthquakes versus magnitude forms a regular function over a very large range of scales (see Fig. 1). When the measure for the earthquake size is the seismic potency or moment (see section “Glossary”), the frequency-size statistics of regional and global earthquakes follow a power law distribution. Precise definitions and details on the seismic potency and moment are given in Aki and Richards (2002) and Ben-Zion (2003). (In this entry, we assume a unit nominal rigidity and will therefore use potency and moment interchangeably.) Omori (1894) found that the decay rate of aftershocks with time follows a power law distribution. One would expect that there might be a simple explanation for why earthquakes occur in a broad range of sizes and follow regular statistical patterns!

In the last two decades, it has become increasingly evident that there are many other systems that respond to slowly changing external conditions with events on extremely large ranges of scales (“crackling noise”). An example of particular interest here involves magnets, which respond to a slowly varying external field by changing their magnetization in a series of bursts or “avalanches” called Barkhausen noise. Just like



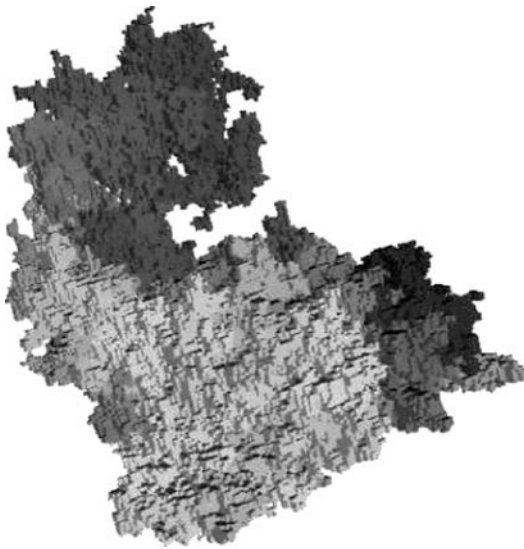
Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems, Fig. 1 Histogram of earthquakes with magnitude 2.0 or larger recorded by the Southern California network during 1984–2002. The earthquake catalog is available at <http://www.data.scec.org/research/SHLK.html>

earthquakes, these avalanches come in many sizes, ranging from microscopic to macroscopic, and are distributed according to a regular function over the entire range. The spectra of the source time function of earthquakes is approximately flat up to a corner frequency related to the rupture size, followed by a power law decay at higher frequencies (Aki and Richards 2002; Ben-Zion 2003). Similarly, the spectra of the number of spins flipping per time during an avalanche in magnets have high frequency power law decay with a low frequency roll-off (Travesset et al. 2002). For certain values of tuning parameters, earthquake and magnet quantities are associated with scale-invariant functions (power laws). In such cases, each individual magnetic avalanche or earthquake slip has a fractal spatial structure (see Fig. 2 for magnets and Fig. 5a for earthquakes). Other systems with similar “collective events” of all available sizes include, among

others, superconductors, charge density waves, and group decision making (Sethna et al. 2001).

While there are several interesting recent reviews, pointing out the similarities between systems with power law event size distributions, the goal of this paper is to develop in detail some of the connections and analysis methods in earthquake and magnetic systems. Expanding on some of our earlier results, we focus especially on the role of disorder and dynamic changes in the strength threshold as potential tuning parameters to drive the system toward power law scaling behavior or away from it. Table 1 summarizes some of the similarities between magnets and earthquakes that are discussed in this review.

In “Models,” we describe several magnet and earthquake models that are simple enough to make the connections transparent and easy to recognize. In “Theoretical Results,” we review theoretical results obtained from these models and their comparison to experimental or observational data. Finally in “Summary,” we summarize the results and discuss future work, both observationally and theoretically, that can help to improve our understanding of the dynamics of earthquakes and magnets.



Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems, Fig. 2 Fractal spatial structure of a medium-sized avalanche of 282,785 domain flips in the three-dimensional random field Ising model (Sethna et al. 2001). Fractal structures and power laws are characteristic of systems at their critical point. The *shading* represents time of the domain flips: the first domains to flip are at the *right* end of the avalanche, the last toward the *left*. The short range of the ferromagnetic interactions causes the avalanche to be spatially connected (see Sethna et al. (2001))

Models

Models for Barkhausen Noise in Magnets

Hysteresis and avalanches in disordered magnetic materials have been modeled using several variants of the nonequilibrium, zero-temperature random-field Ising model (RFIM), which is one of the simplest models of magnetism, with applications far beyond magnetic systems (for a review, see Sethna et al. (2001) and also Dahmen (1995), Nattermann (1997), and Perković et al. (1995)). In contrast to some other hysteresis models, like the Preisach model (Mayergoyz 1991) and the Stoner-Wohlfarth model (Jiles 1991), where interactions between the individual hysteretic units (grains) are not included and collective behavior in the form of avalanches is not addressed, in the RFIM the inter-grain coupling is an essential feature and cause for hysteresis and avalanche effects.

Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems, Table 1 Some scaling features that are similar for magnets and earthquakes. More

	Earthquake system	Magnetic system
Frequency-size statistics	Power law near criticality, characteristic distribution away from criticality (“ Results on the Monotonic Version of the Model ”)	Same as earthquakes (“ Results on the Monotonic Version of the Model ”)
Scaling of source shape functions	Parabola for moment rate shape of events with fixed duration T in simulations, scaling function skewed to the left for observational data (“ Moment Rate Shapes for Monotonic Models ”)	Same as earthquakes (“ Moment Rate Shapes for Monotonic Models ”)
Spatial properties of individual events	Fractal near criticality, compact away from criticality (“ Non-monotonic Models ” and Fig. 5)	Same as earthquakes (“ Non-monotonic Models ” and “ Phase Diagram ” and Fig. 2)
Spectral decay of source function of individual events	Flat up to a corner frequency followed by power law decay (“ Introduction ”)	Same as earthquakes (“ Introduction ”)

details on the various properties are given in the indicated sections

The Random Field Ising Model (RFIM)

The *equilibrium* RFIM was originally introduced to study disordered magnetic materials in thermal equilibrium. We study the *nonequilibrium* version, to model hysteresis and avalanches observed *far from thermal equilibrium*. Even though the model is a toy version of the microscopic details in a magnet, near the critical point, it correctly describes the large-scale behavior of systems with the same general properties such as symmetries, dimensions, interaction ranges, and dynamics (Dahmen 1995), as follows from renormalization group arguments.

In the RFIM, to each site i in a simple cubic lattice is assigned a variable s_i , a so-called spin, which can take two different values, $s_i = +1$ (“up”) or $s_i = -1$ (“down”). (This corresponds to a real magnet where a crystal anisotropy prefers the magnetic moments or elementary domains, represented by the spins, to point along a certain easy axis.) Each spin interacts with its nearest neighbors on the lattice through a positive exchange interaction, J_{nn} , which favors parallel alignment. (For the behavior on large scales, the exact range of the microscopic interaction is irrelevant, so long as it is finite.) Some variations of the RFIM also include *long-range* interactions due to the demagnetizing field and the dipole-dipole interactions. A general form of the Hamiltonian can be written as (Kuntz and Sethna 2000)

$$\mathcal{H} = -\sum_{nn} J_{nn} s_i s_j - \sum_i H s_i - \sum_i h_i s_i + \sum_i \frac{J_{inf}}{N} s_i - \sum_{\{i,j\}} J_{dipole} \frac{3 \cos(\theta_{ij}) - 1}{r_{ij}^3} s_i s_j, \quad (1)$$

where H is the homogeneous external magnetic driving field; h_i is a local, uncorrelated random field, that models the disorder in the system; J_{inf} is the strength of an infinite range demagnetizing field; N is the total number of spins in the system; and J_{dipole} is the strength of the dipole-dipole interactions. The power laws of generated events are independent of the particular choice for the distribution $\rho(h_i)$ of random fields, for a large variety of distributions. Usually, a Gaussian distribution of random fields is used, with a standard deviation (“disorder”) R . As a simple approximation, the model is studied at zero temperature, far from equilibrium, to describe materials with sufficiently high barriers to equilibration, so that temperature fluctuations are negligible on experimental time scales. As the magnetic field is adiabatically slowly changed between $H = -\infty$ and $H = +\infty$, two different *local* dynamics have been considered:

1. In the first (“bulk”) dynamics, each spin s_i flips while decreasing its own energy. We have studied this dynamics for the original RFIM

without long-range interactions, i.e., for $J_{\text{inf}} = J_{\text{dipole}} = 0$ (Dahmen 1995; Perković et al. 1995). This dynamics allows for *both* domain nucleation (when a spin s_i surrounded by equal valued spins flips in the opposite direction) *and* for domain wall motion (when a spin flips on the surface of a preexisting cluster of uniform spins in a background of opposite valued spins). A spin flip can trigger neighboring (or more generally, coupled) spins to flip as well, leading to an avalanche of spin flips, analogous to a real Barkhausen pulse. During an avalanche, the external field is kept constant until the avalanche is finished, in accordance with the assumed adiabatic limit. The model is completely deterministic – two successive sweeps through the hysteresis loop produce the exact same sequence of avalanches (since the temperature is set to zero). This dynamics may be appropriate to describe, for example, hard magnetic materials with strong anisotropies. The analog earthquake system may be associated with fault regions or fault networks that have strong geometrical and material heterogeneities.

2. The second dynamics is a “front propagation dynamics” in which only the spins on the edge of an existing front (interface between up and down spins) flip if that decreases their energy. This dynamics can be used to model soft magnetic materials with a single or several non-interacting advancing domain walls and negligible new domain nucleation, due to anti-ferromagnetic demagnetizing fields. The front propagation model without long-range interactions ($J_{\text{inf}} = J_{\text{dipole}} = 0$) was originally introduced by Robbins et al. to model fluids invading porous media (Martys et al. 1991). The analog earthquake system for this case may be associated with a single fault zone.

Simple Models for Inhomogeneous Earthquake Faults

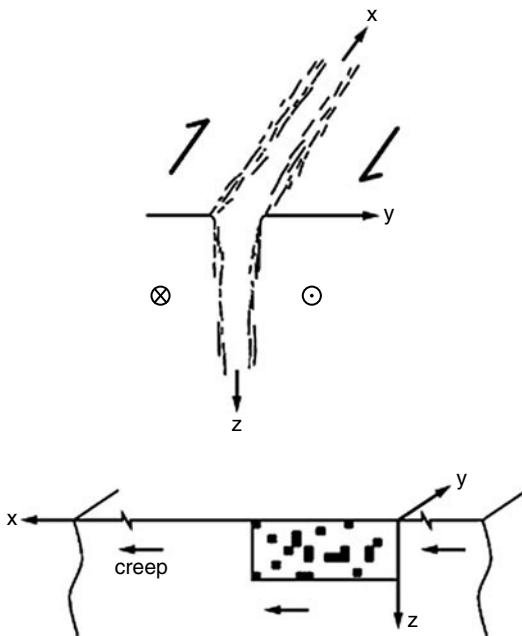
Much of the previous work on simple earthquake models has involved variants of the Burridge-Knopoff (or “slider-block”) model, in which complex behavior is generated in a system with many degrees of freedom and where inertia, friction laws,

and inherent discreteness play important roles (Carlson et al. 1994; Langer et al. 1996; Rice and Ben-Zion 1996). These systems appear to exhibit power law statistics over some range with a cutoff beyond some magnitude and with most of the slip occurring in larger system-size events. However, the understanding of the origin of the power law behavior is limited. Our approach here is to obtain an analytic understanding of a class of models and then to add in various additional features by analytic scaling arguments using tools from the theory of phase transition and the renormalization group, aided by numerical studies. There are interesting related studies using tools from statistical physics (Chen et al. 1991; Schwarz and Fisher 2001). Some studies suggest that the power law scaling is connected to a spinodal (Klein et al. 1997). Various cellular automata models have also been used for modeling earthquakes (Lomnitz-Adler 1993). Rather than reviewing a large number of models, we will focus on a subgroup of models that we found particularly well suited to clarify the connection between earthquake and magnetic systems with a jerky response to slowly changing external conditions.

The Ben-Zion and Rice Model

A representative of the class of models that we consider is a model developed originally by Ben-Zion and Rice (Ben-Zion 1996; Ben-Zion and Rice 1993, 1995), referred to below as the BZR model. The model assumes that a narrow irregular strike-slip fault zone of horizontal length L and vertical depth W may be represented by an array of $N \sim LW$ cells in a two-dimensional planar region of length L and width W , with long-range interaction, abrupt transitions in the threshold dynamics during failure, and constitutive parameters that vary from cell to cell to model the disorder (offsets, etc.) of the fault zone structure (Fig. 3).

The cells represent brittle patches on the interface between two tectonic blocks that move with slow transverse velocity v in the x direction at a great distance from the fault. The interaction between cells during slip events is governed by 3D elasticity and falls off with a distance r from the failure zone as $1/r^3$. The cells remain stuck while the stress τ_i on each cell is increased



Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems, Fig. 3 Illustration of the Ben-Zion and Rice (BZR) model: projection of a 3D fault zone (top) onto a 2D interface embedded in a 3D elastic half space (bottom). The geometrical inhomogeneities of the physical fault zone are modeled by spatially varying constitutive parameters of the brittle patches (see Mehta et al. (2006))

gradually as a result of the external loading which grows adiabatically (i.e., we take the limit $\nu \rightarrow 0$). When the stress on a cell i reaches its local failure threshold $\tau_{s,i}$, the cell slips until the stress is reduced to its local arrest stress $\tau_{a,i}$. Both failure stress and arrest stress are distributed according to some bounded probability distribution. The stress drop resulting from a cell failure is redistributed to the other cells according to the long-range elastic stress transfer function. The resulting stress increase on the other cells can cause some of them to slip as well, leading to an avalanche of cell slips, or a model earthquake. A review of extensive numerical simulations with various versions of the BZR model, in relation to observed features of seismicity, criticality, and other dynamic regimes, is given in Zöller et al. (2009).

Dynamic Weakening The model includes dynamic weakening effects during the failure

process (Ben-Zion 1996; Ben-Zion and Rice 1993, 1995): after an initial slip in an earthquake, the strength of a failed cell is reduced to a *dynamic* value:

$$\tau_{d,i} \equiv \tau_{s,i} - \epsilon(\tau_{s,i} - \tau_{a,i}), \quad (2)$$

with $0 \leq \epsilon \leq 1$ parametrizing the relative importance of the dynamic weakening in the system. This weakening represents the transition from static friction to dynamic friction during the rupture. The strength of a failed cell remains at its dynamic value throughout the remainder of the earthquake. In the time intervals between earthquakes, all failure thresholds heal back to their static value $\tau_{s,i}$.

Dynamic Strengthening The model can be expanded further to include dynamic strengthening represented by $\epsilon < 0$. Multidisciplinary observations indicate (Ben-Zion and Sammis 2003) that brittle failure of rock has an initial transient phase associated with strengthening, distributed deformation, and creation of new structures. Detailed frictional studies also show an initial strengthening phase associated with the creation of a new population of asperity contacts (Ben-Zion 2003; Dieterich 1979). In mean field studies of our model (Fig. 3) discussed in “Results on Aftershocks,” we associate $\epsilon < 0$ with regions off the main fault segments that are in an early deformation stage. The events that are triggered as the failure stresses are lowered back in the following weakening period are referred to as *after-shocks*. The Omori law (Ben-Zion 2003; Utsu 2002; Utsu et al. 1995) is obtained if we assume that the increased failure stress thresholds $\tau_{f,i}$ are slowly lowered with time as $\log(t)$ toward their earlier static values $\tau_{s,i}$ and that the stresses are distributed over a wide range of values (Mehta et al. 2006).

Related General Continuum Equations of Motion

The above model is a special case of a more general class of models for infinite systems driven by a constant drive force F (Fisher et al. 1997). We consider general equations of motion of the form

$$\eta \partial u(\mathbf{r}, t) / \partial t = F + \sigma(\mathbf{r}, t) - f_R[u(\mathbf{r}, t), \mathbf{r}, \{u(\mathbf{r}, t') < 1\}] \quad (3)$$

where

$$\sigma(\mathbf{r}, t) = \int_{-\infty}^t dt' \int d^d \mathbf{r}' J(\mathbf{r} - \mathbf{r}', t - t') [u(\mathbf{r}', t') - u(\mathbf{r}, t)] \quad (4)$$

is the stress and f_R is a quenched random “pinning” force crudely representing inhomogeneities in the friction, asperities, stepovers, etc., which in general can depend on the local past history (e.g., as in velocity-dependent friction). The dynamic variables $u(\mathbf{r}, t)$ are assumed to represent the discontinuity across the fault plane in the component of the displacement in the direction of slip. The dynamics depend on the local history dependence of the pinning force, the stress transfer function $J(\mathbf{r}, t)$, and the coefficient η that represents the fault impedance. (In an elastic medium, the impedance depends on mass density, the elastic parameters, and directional parameters (Aki and Richards 2002).) Equation 3 can be considered a continuum description of the rules of the BZR model. Integrating out the degrees of freedom due to the bulk material on either side of the $d = 2$ -dimensional fault plane leaves us with effective long-range static stress transfer: $J_s(r) \equiv \int dt J(r, t) \sim 1 / r^{d+\Gamma} \sim 1/r^3$. For a planar fault in an elastic half space, $d = 2$ and $\Gamma = 1$ (Ben-Zion 1996; Ben-Zion and Rice 1995). The correlations in f_R are generally assumed to be short range in u and $\mathbf{r}$. (For results on the BZR model with long-range correlations in the disorder, see Ben-Zion (1996), Fisher et al. (1997), Zöller et al. (2005), and section “Theoretical Results.”) In a version of the BZR earthquake model with a constant driving force F , the loading may be replaced by driving through a weak spring with spring constant $K \sim 1/L$ coupled to the slowly moving continents far away (i.e., replacing F in Eq. 3 by $F(\mathbf{r}, t) = K[v t - u(\mathbf{r}, t)]$, with $v \rightarrow 0$).

Monotonic Models Substantial simplifications occur if f_R is history independent and

$J(\mathbf{r}, t) \geq 0$ for all $(\mathbf{r}, t)$, leading to *monotonic* models (Fisher et al. 1997). Related monotonic models have been studied extensively in various other contexts (Ertaş and Kardar 1994b; Narayan and Fisher 1992b). Examples include elastic depinning models for contact lines, vortex lines, liquids invading porous materials, and elastic charge density waves. Their crucial simplifying feature is that the steady-state velocity $\bar{v} \equiv \langle \partial u / \partial t \rangle$ is a history-independent function of F (Middleton 1992). In the context of the BZR model, this corresponds to the case with zero weakening ($\epsilon = 0$) and nonnegative J . A crucial feature of monotonic models is that the slip profile $\Delta u(\mathbf{r})$ of a quake is *independent of the dynamics* (Middleton 1992). However, several interesting dynamic issues discussed below are associated with the effects left out of the monotonic models that can make this feature break down.

Non-monotonic Models

(a) *Weakening*: We first consider including some weakening effects of sections which have already slipped in a given quake. This is best studied in the discrete model. In analogy to the dynamic weakening in the BZR model discussed above, we choose (Fisher et al. 1997)

$$f_R = \tilde{f}_R[u(\mathbf{r}), \mathbf{r}] \{1 - \epsilon \Theta[u(\mathbf{r}, t) - u(\mathbf{r}, t - T)]\} \quad (5)$$

with T a cutoff time much longer than the duration of the largest quakes but much smaller than the interval between the quakes. Here $\Theta(x)$ is the Heaviside step function. As mentioned, the case $\epsilon > 0$ represents the difference between static and dynamic friction. The effects of small weakening ($\epsilon > 0$) can be analyzed perturbatively (see section “Theoretical Results”).

(b) *Stress Pulses*: A similar but more subtle effect can be caused by stress pulses that result from nonpositive $J(\mathbf{r}, t)$; these arise naturally when one includes elastodynamic effects. We consider

$$J(\mathbf{r}, t) \sim \frac{\delta(t - \frac{r}{c})}{r^d + \Gamma} + \frac{\alpha \delta'(t - \frac{r}{c})}{cr^{d+\gamma}} \quad (6)$$

with c the sound speed, $\delta(t)$ the Dirac delta distribution, and $\delta'(t) = d\delta(t)/dt$. The scalar approximation to elasticity in a half space corresponds to $d = 2$, $\Gamma = 1$, $\gamma = 0$, and $\alpha = 1$ (Fisher et al. 1997). If a region slips forward, the stress at another point first has a short pulse at the sound arrival time from the second term in Eq. 6 and then settles down to its smaller static value, i.e., it is non-monotonic. The magnitude of these stress pulses and their duration are set by various aspects of the models; for example, larger η in Eq. 3 implies weaker stress pulses as the local motion will be slower.

Theoretical Results

Both the magnet and earthquake models of the previous section are capable of producing a large range of power law scaling of event sizes and related scale-invariant quantities in response to a slowly varying driving force or field. This section highlights similarities between these different physical systems and attempts to explain them.

The Universality Class of the BZR Model

We first review results for the simplified monotonic case, starting with scaling relations for driving with fixed force and far field plate motion and continuing with moment rate shapes. We then discuss additional results associated with non-monotonic versions of the model, including mode switching and aftershocks.

Results on the Monotonic Version of the Model

General Results: Depinning Transition As mentioned above, substantial simplifications occur for the monotonic version of the model, i.e., if f_R is history-independent and $J(\mathbf{r}, t) \geq 0$ for all $(\mathbf{r}, t)$. In Ertaş and Kardar (1994b), Fisher et al. (1997), and Narayan and Fisher (1992b), it is shown that for F greater than a critical force F_c , the displacement grows continuously in a “sliding

state” for which the mean velocity $\bar{v} \equiv \langle \partial u / \partial t \rangle \sim (F - F_c)^\beta$. Here, β is a universal exponent that is independent of the microscopic details of the system. It only depends on a few fundamental properties, such as symmetries, spatial dimensions d , range of interactions, etc. (Narayan and Fisher 1992b). Longtime dynamic properties such as β depend in addition on the small ω dependence of $J(\mathbf{q}, \omega)$ (Narayan and Fisher 1993).

For F less than the critical force F_c , the mean velocity is $\bar{v} \equiv 0$. If F is adiabatically slowly increased toward F_c , the system moves from one metastable configuration to another by a sequence of “quakes” of various sizes. The “quakes” can be characterized by their radius R , the d -dimensional area A which slips (by more than some small cut-off), their potency or moment $M \equiv \int_A d^d \mathbf{r} \Delta u(\mathbf{r})$, a typical displacement $\Delta u \sim M/A$, and a duration τ . The critical force F_c marks a second-order phase transition point. Such phase transitions are typically associated with power law scaling behavior.

In the class of earthquake models with long-range interactions along the fault involving the static stress transfer $J_s(r) \equiv \int dt J(r, t) \sim 1/r^3$, the equations are very similar to those of a model for contact line depinning studied in Ertaş and Kardar (1994b). Using renormalization group methods, it was shown in Ertaş and Kardar (1994b) that for a physical two-dimensional interface (or “fault”) in a three-dimensional elastic half space, these long-range interactions are so long that the scaling behavior near F_c is correctly described by mean field theory (up to logarithmic corrections, since $d = 2$ is the “upper critical dimension”). The main assumption in mean field theory is that the spatial and temporal fluctuations in the displacement field $u(\mathbf{r}, t)$ are so small that the local displacement $u(\mathbf{r}, t)$ can be replaced by a time-dependent spatial average $u(t)$, which then needs to be determined self-consistently from the behavior of the neighboring regions that contribute to the stress at a chosen point $\mathbf{r}$ (Fisher 1998). The same mean field equations are obtained when the long-range interaction is approximated to be constant in space $J(\mathbf{r}, t) = J_{\text{mfi}}(t)/(LW)$. With this approximation, Eqs. 3 and 4 become

$$\begin{aligned} \eta \partial u(\mathbf{r}, t) / \partial t \\ = F + \sigma_{mfi}(\mathbf{r}, t) - f_R[u(\mathbf{r}, t), \mathbf{r}, \{u(\mathbf{r}, t') < t\}] \end{aligned} \quad (7)$$

where

$$\sigma_{mfi}(\mathbf{r}, t) = \int_{-\infty}^t dt' J_{mfi}(t - t') [u(t') - u(\mathbf{r}, t)] \quad (8)$$

and the self-consistency requirement is

$$\int u(\mathbf{r}, t) d^2r / (LW) = u(t) \quad (9)$$

Many scaling exponents and scaling functions can be calculated exactly in mean field theory by solving these simplified equations of the model. In Dahmen (1995), Fisher (1998), and Marchetti et al. (2000), several illustrative examples are given for solving similar self-consistent mean field theories. There are various approaches that one may use, ranging from numerical simulations to analytic expansion and scaling analysis near a phase transition point where universal power law scaling occurs. The approach of choice to solve the mean field equations depends on the quantity under consideration. To obtain the exact results for the scaling behavior of the frequency-size statistics of earthquake or avalanche events, a fairly simple approach is to use a discrete version of the model in which we treat the fault as a discrete set of dislocation patches, coupled to a mean displacement and an external driving force that slowly increases with time. (The stress τ_i at each patch is given by Eq. 16 of “Mode Switching” below.) As shown in Dahmen et al. (1998), the sequence that describes the distance from failure of the rescaled stress variables resembles a biased random walk. The scaling behavior of the resulting random walk is known exactly from the literature. Using this mapping, it then becomes straightforward to derive universal scaling predictions for the mean field earthquake frequency-size distribution (Dahmen et al. 1998).

Furthermore, as shown in Cizeau et al. (1997) and Ertaş and Kardar (1994b), their (and thus also our) model have the same scaling behavior as a front propagation model for a two-dimensional domain wall in a soft magnet with long-range dipolar magnetic interactions, driven by a slowly changing external field (see section “Models”). A flipping spin in the magnet model corresponds to a slipping dislocation patch in the earthquake model. The long-range elastic interactions in the earthquake model are similar to the long-range dipolar magnetic interactions in the magnet model. The driven two-dimensional magnetic domain wall in the (three-dimensional) magnet model corresponds to the driven two-dimensional earthquake fault in a three-dimensional elastic half space. Since the scaling behavior of the earthquake model and that of Ertaş and Kardar (1994b) and Zapperi et al. (1998) are identical, we may simply copy their results and translate them into quantities that can be extracted from seismic data. Using tools from phase transitions, such as the renormalization group (RG), near the critical force, the following scaling results were derived by Cizeau et al. (1997), Ertaş and Kardar (1994b), Narayan and Fisher (1992b, 1993, Zapperi et al. (1998) and others:

$$\begin{aligned} \Delta u &\sim R^\zeta, \\ A &\sim R^{d_f} \text{ with } d_f \leq 2 \text{ a fractal dimension,} \\ M &\sim R^{d_f + \zeta}, \\ \text{and } \tau &\sim R^z. \end{aligned}$$

The differential distribution $P(M)$ of moments M is shown in Ertaş and Kardar (1994b), Narayan and Fisher (1993), Fisher (1998), Fisher et al. (1997) to scale as

$$P(M) dM \sim dM / M^{1+B} \rho_\infty(M/\hat{M}) \quad (10)$$

with ρ_∞ as a universal scaling function which decays exponentially for large argument. The cut-off $\hat{M}$ for large moments is characterized by a correlation length – the largest likely radius – $\xi \sim 1/(F_c - F)^\nu$ with $\hat{M} \sim \xi^{d_f + \zeta}$.

In the same references, it is shown that in mean field theory, $B = 1/2$, $1/\nu = 1$, $z = 1$, and the

quakes are fractal with displacements of order the range of correlations in $f_R(u)$, i. e. $\zeta = 0$.

These mean field exponents are valid for a $d = 2$ -dimensional planar fault in a three-dimensional elastic half space (Ben-Zion and Sammis 2003), since the physical fault operates at the upper critical dimension. As usual, at the upper critical dimension, there are logarithmic corrections to mean field results. Using renormalization group methods, one can calculate these corrections (Fisher et al. 1997) and finds barely fractal quakes with $A \sim R^2 / \ln R$ so that the fraction of the area slipped decreases only as $1/\ln r$ away from the “hypocenter.” The typical slip is $\Delta u \sim (\ln R)^{1/3}$ so that $M \sim R^2 / (\ln R)^{2/3}$. The scaling form of $P(M)$ is the same as Eq. 10 with the mean field ρ_∞ , although for $M \ll \hat{M}$, $P(M) \sim (\ln M)^{1/3} / M^{3/2}$ so that B will be virtually indistinguishable from $1/2$ (Fisher et al. 1997). A similar form of moment distribution and exponent value $B = 1/2$ were obtained also for a critical stochastic branching model (Vere-Jones 1976).

More Realistic Driving of a Fault We now consider more realistic drive and finite-fault-size effects. As mentioned, driving the fault by very slow motion far away from the fault is roughly equivalent to driving it with a weak spring, i.e., replacing F in Eq. 3 by $F(\mathbf{r}, t) = K[v\tau - u(\mathbf{r}, t)]$. With $v \rightarrow 0$, the system must then operate with the spring stretched to make $F(\mathbf{r}, t) \leq F_c$ at least

on average, to ensure $\bar{v} = 0$; depending on the stiffness of the spring, it will actually operate just below F_c , as shown below. If in constant force drive the force is increased by a small amount ΔF , the average resulting slip per area, $\langle \Delta u \rangle \equiv \sum_i \Delta u_i / (LW)$ is given by the total

potency/moment per total area $M \equiv \int d^d \mathbf{r} \Delta u(\mathbf{r}) / (LW)$. The total moment per area observed in response to a small force increase equals the number $n\Delta F$ of earthquakes per area that are triggered by the increased ΔF , multiplied with the average observed moment of a single earthquake $\langle M \rangle = \int MP(M)dM$. The result is

$$\langle \Delta u \rangle = n\Delta F \int MP(M)dM \quad (11)$$

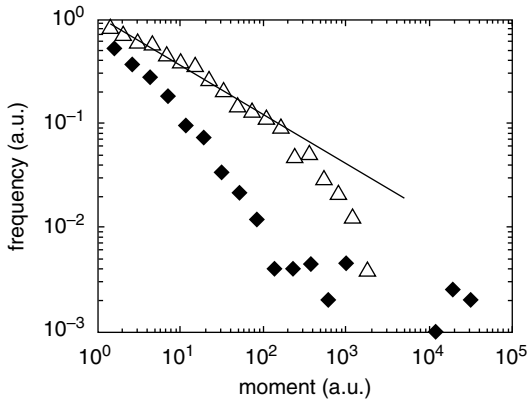
where n is the number of quakes per unit area per force increase ΔF . It has been shown that $n(F)$ is non-singular at F_c (Narayan and Fisher 1992b), so it can be treated like a constant near F_c . Plugging in Eq. 10 and the scaling laws written above and below that equation, we obtain

$$\langle \Delta u \rangle \sim \Delta F \xi^{(2\tilde{\Gamma} + \zeta)(1-B)} \sim \Delta F \xi^\zeta \quad (12)$$

for our case where mean field results can be used for the critical exponents. For consistency, we must have in steady state with the spring drive $Kv\Delta t = \Delta F = K\Delta u$ so that the system will operate with a correlation length $\xi \sim 1/K^{1/\tilde{\Gamma}}$, i.e., $1/K$ for our case. For a fault section with linear dimensions of order L , the drive either from uniformly moving fault boundaries or from a distance $\sim L$ perpendicularly away from the fault plane will be like $K \sim 1/L$, so the power law quake distribution will extend out to roughly the system size $\xi \sim L$. For smaller quakes, i.e., $R \ll L$, the behavior will be the same as in the infinite system with constant F drive, but the cutoff of the distribution of moments will be like Eq. 10 with a different cutoff function ρ that depends on the shape of the fault, how it is driven, and the boundary conditions.

We have tested these conclusions numerically by simulating the BZR model, which is a discrete space, time, and displacement version of a monotonic Eq. 3, with quasistatic stress transfer appropriate for an elastic half space (Ben-Zion 1996; Ben-Zion and Rice 1993). The slip, u , is purely in the horizontal direction along the fault, and $f_R[u(\mathbf{r})]$ is a series of equal-height spikes with spacings which are a random function of $\mathbf{r}$. When $\sigma(\mathbf{r}, t) > f_R[u(\mathbf{r}, t)]$, $u(\mathbf{r})$ jumps to the next spike. This provides a way of implementing the random stress drops of the BZR model. The boundary conditions on the bottom and sides are uniform creep or slip ($u = v\tau$) with infinitesimal v – and stress-free on the top (Fig. 3). The statistics of the moments of the quakes are shown by the triangles in Fig. 4. Although the uncertainties are

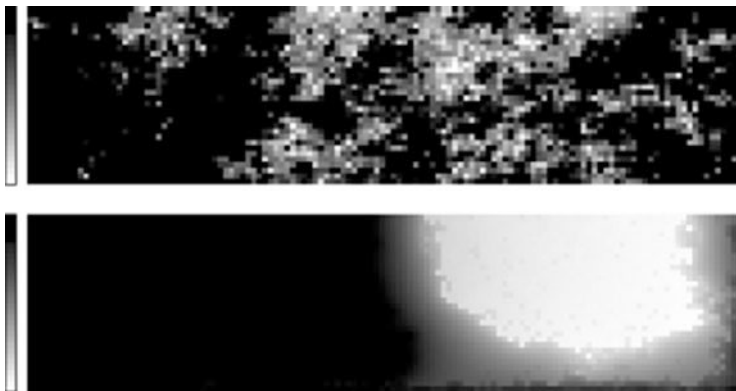
appreciable, relatively good agreement is found with the prediction $B = 1/2$. One typical large quake is illustrated in Fig. 5 (top); it appears almost fractal as predicted and tends to stay away from the bottom and sides due to the specific



Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems, Fig. 4 Histograms of moments for a simulation of a rectangular fault with 32×128 cells for the discrete monotonic quasistatic model (with arbitrary units (a.u.)). *Triangles*: without dynamic weakening ($\epsilon = 0$). *Diamonds*: with dynamic weakening of $\epsilon = 0.95$. (ϵ is defined in Eq. 5.) The *straight line* indicates the predicted slope $B = 1/2$ (From Fisher et al. (1997))

loading that we chose. The ratios of the moments of quakes to their areas have been studied and found to grow only very slowly with the area, as predicted from the logarithmic corrections listed below Eq. 3. This is in striking contrast to earthquakes in conventional crack models which are compact (Fig. 5 (bottom)) and have $\Delta u \sim R$ (i.e., $\zeta = 1$), so that $M/A \sim \sqrt{A}$. As discussed by Ben-Zion and Zhu (2002), however, the scaling $M \sim A$ appears to be consistent with observational results for small earthquakes which presumably propagate and are arrested in rough stress fields. More observational data on the scaling of the moment M with the slipping area A for smaller earthquakes would be highly desirable to test this prediction more precisely.

Because the system is at its critical dimension, the cutoff function ρ of the moment distribution appropriate to the boundary conditions, as well as various aspects of the shapes and dynamics of quakes, can be computed using tools from the theory of phase transitions (Fisher 1998; Fisher et al. 1997). For quasistatic stress transfer, $J(\mathbf{r}, t) \sim \delta(t)/r^3$, in the infinite system, the quake durations are found to scale as $\tau \sim R^z$ with $z = 1$ for a $d = 2$ -dimensional fault, with logarithmic corrections (Ertaş and Kardar



Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems, Fig. 5 Distribution of horizontal slip, u , along a fault with 32×128 cells for a *single* large quake event. *Lighter shading* represents larger slip during the quake. *Top*: almost fractal quake with a total moment of 1,750 (and 1,691 cells failing) for the monotonic

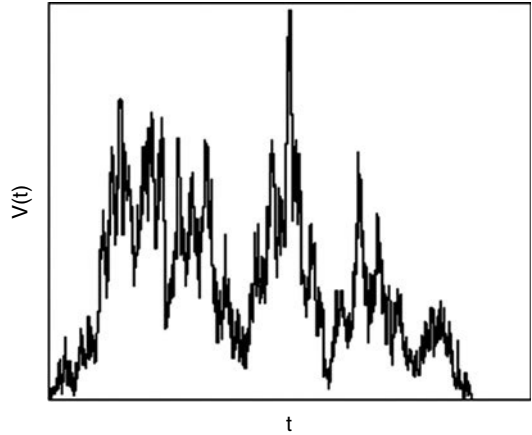
model without any dynamic effects ($\epsilon = 0$). *Bottom*: “crack-like” quake with a total moment of 16,922 (and 2,095 cells failing) for the model with dynamic weakening ($\epsilon = 0.95$). In both cases, the system is driven by horizontally creeping fault boundaries (*sides* and *bottom*) while the top boundary is free (From Fisher et al. (1997))

1994b). (A more physical dynamics with sound-travel-time delay has slower growth of the quakes with $z = 1$ in all dimensions.) Due to the geometrical disorder included in the model, in either case, the growth will be very irregular – including regions starting and stopping – in contrast to crack models and what is often assumed in seismological analysis of earthquakes on more regular faults. Similar fractal-like quakes were simulated by Zöller et al. (Zöller et al. 2009; Zöller et al. 2004), for a quasi-dynamic version of the BZR model that includes stress redistribution with a finite communication speed.

Moment Rate Shapes for Monotonic Models

In both magnet and earthquake models, it has been shown that there are not just universal scaling exponents but also some experimentally accessible universal scaling functions (Sethna et al. 2001). By comparing theoretical predictions for these functions to experiments or observations, one can often test models much more accurately than by merely comparing a finite set of discrete exponents. Two such functions were first discovered for Barkhausen noise in magnets (Mehta et al. 2002; Sethna et al. 2001). The analogy between magnets and earthquakes then leads to the development of the corresponding functions for earthquakes. For slowly driven magnets, consider the time history $V(t)$ of the number of domains flipping per unit time (Barkhausen train). It is called V because it is usually measured as a voltage in a pickup coil. An example of a Barkhausen train for a single avalanche is shown in Fig. 6.

The voltage function $V(t)$ in magnets is the analog of the moment rate $dm/dt(t)$, or the slip per unit time for earthquakes. Recent analysis allowed researchers to obtain the moment rate $dm_0(t)/dt$, during the propagation of earthquake rupture for hundreds of large seismic events recorded on global networks (Bilek 2001; Houston 2001). The moment rates shown below are derived from inversions of teleseismically recorded seismogram on a global seismic network (Ruff and Miller 1994). (The frequency-moment distribution $D(M_0) \sim M_0^{-1-\beta}$ of the observed data (Bilek 2001) has three decades of scaling



Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems, Fig. 6 Voltage train of a typical large avalanche. Note that the voltage fluctuates drastically and the avalanche nearly stopped several times (From Kuntz and Sethna (2000)). The analogous moment rate time trace for earthquakes (though measured with lower resolution) is shown in the *right inset* marked “RAW” of Fig. 8

and an exponent of $\beta = 1/2 \pm 0.05$, in close agreement with the BZR model near $\epsilon = 0$ (Mehta et al. 2006).)

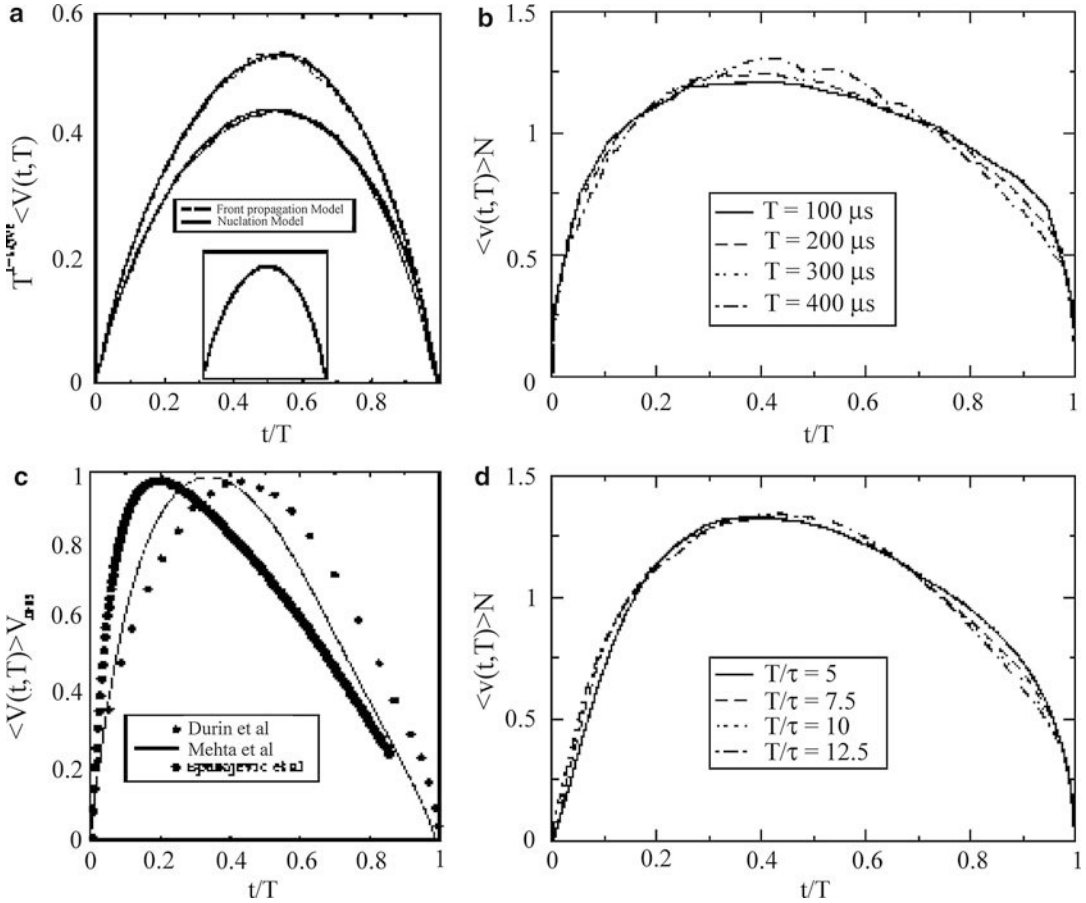
For both magnets and earthquakes, there are large fluctuations in $V(t)$ and $dm/dt(t)$, respectively (Fig. 6). However, averaging the signal over many avalanches leads to typical shapes. Figure 7 shows the average over all avalanches of fixed duration T , $\langle V \rangle(T, t)$ obtained from simulations of two variants of the RFIM (a) and from three different Barkhausen noise experiments (b). Figure 8 shows $\langle dm/dt \rangle(T, t)$ obtained for the BZR earthquake model and derived from earthquake observations, respectively. The renormalization group and scaling theory (Sethna et al. 2001) predict that for a self-similar system at a critical point with power law size and duration distributions for avalanches, there are self-similar average avalanche profiles. As shown in Mehta et al. (2006) and Sethna et al. (2001), one finds

$$\langle dm/dt \rangle(T, t) \sim T^{b'} g(t/T) \quad (13)$$

where the function $g(x)$ is a universal scaling prediction and $b' \equiv 1/(\sigma v z) - 1 = 1$ for the BZR earthquake model (as obtained from mean

field theory). The corresponding value for b' for magnets in three dimensions is smaller – the values used for the corresponding collapses can be read off for the different versions of the RFIM from the caption of Fig. 7.

Based on universality, one would expect these theoretical predictions to agree with experimental results, apart from an overall shift in time and voltage or moment rate scales. For the moment rate of earthquakes, this means



Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems, Fig. 7 (a) **Theoretical average avalanche shape scaling functions for fixed avalanche durations T** denoted with $g(t/T)$ in the text, for the nucleation and the front propagation RFIM (Mehta et al. 2002). The overall height is nonuniversal; the curves for the two models are otherwise extremely similar. The front propagation model has $1/vz = 1.72$, and the nucleation model has $1/\sigma vz = 1.75$ in this collapse. The *inset* shows the two curves rescaled to the same (nonuniversal) height: the two curves are quantitatively different but far more similar from one to another than either is to the experimental curve in (b). (b) **Experimental average pulse shapes from three different experiments** for fixed pulse duration, as measured by three different groups (Durin and Zapperi 2000, 2002; Mehta et al. 2002;

Spasojevic et al. 1996). Notice that both theory curves are much more symmetrical than those of the experiments. Notice also that the three experiments do not agree. At first, this result represented a serious challenge to the idea about universality of the dynamics of crackling noise (Sethna et al. 2001). (c) **Pulse shape asymmetry experiment** (Zapperi et al. 2005). Careful experiments show a weak but systematic duration dependence in the collapse of the average Barkhausen pulse shape. The longer pulses (larger avalanches) are systematically more symmetrical (approaching the theoretical prediction). (d) **Pulse shape asymmetry theory** (Zapperi et al. 2005). Incorporating the delay effects of eddy currents into the theoretical model produces a similar systematic effect. The nonuniversal effects of eddy currents are in principle irrelevant for extremely large avalanches (From Sethna (2006))

$$\langle dm/dt \rangle_{\text{observation}}(T, t) = A \langle dm/dt \rangle_{\text{theory}}(T/B, t/B) \quad (14)$$

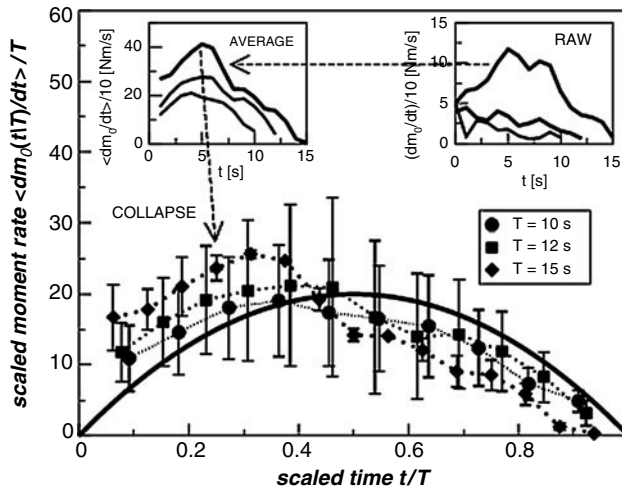
for some rescaling factors A and B and similarly for the average voltage $\langle V \rangle(t, T)$ in magnets. In both cases, the theory predicts a symmetrical-looking profile. The mean field prediction for $g(x)$ is in fact a parabola (Mehta et al. 2006; Sethna et al. 2001) – the theoretical prediction thus is that events grow as quickly as they decay. As seen in Figs. 7b and 8, the experimental/observational profile in both cases, however, appear skewed – the real events tend to grow more quickly than they decay! A similar asymmetry has also been observed in avalanches associated with plastic deformation (Laurson and Alava 2006).

For magnets, this apparent disagreement has been resolved by taking greater account of a microscopic detail involving eddy currents that had been neglected by previous models. Eddy currents are transient current loops that arise in conducting magnets in response to the reorientation of a magnetic domain. These currents temporarily prevent neighboring domains from being triggered to

realign in the same direction in an avalanche of domain reversals. The eddy currents decay after a microscopic time τ given by the resistance of the material. Their delay effect thus also decays after a time τ . If the avalanche duration is large compared to τ , this effect is negligible and the mean profile approaches the predicted symmetrical shape (see Fig. 7c and d).

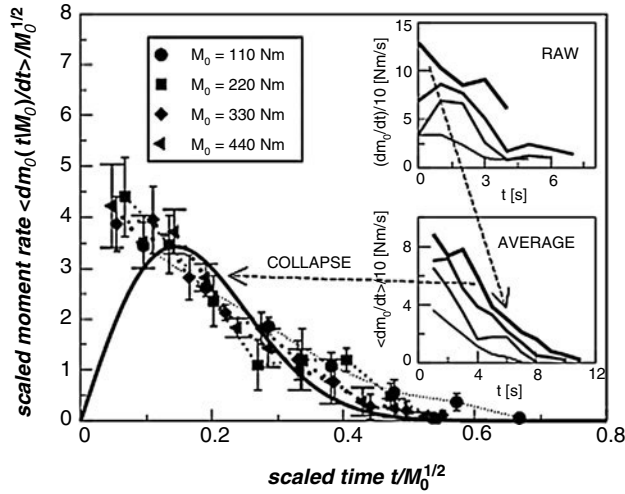
The source of asymmetry in the mean moment rate profile may be similar for earthquakes (Dahmen 2005). It has been suggested that triggering delays – arising from a noticeable earthquake nucleation time or an increase in the failure threshold during the formation of new cracks and subsequent weakening as rock damage increases – could be responsible for aftershocks that often follow large earthquakes (Mehta et al. 2006). On long time scales, a large mainshock with smaller aftershocks can be seen as a similar asymmetry to that seen in magnets, possibly with a similar explanation.

There is a second scaling function that may be extracted from the same data: Fig. 9 shows the average over all earthquakes of fixed total moment



Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems, Fig. 8 A collapse of averaged earthquake pulse shapes, $\langle dm_0(t|M_0)/dt \rangle$ with a duration of T (seconds) within 10 % (given in legend), is shown. The collapse was obtained using the mean field scaling relation (Kuntz and Sethna 2000): $\langle dm_0(t/T)/dt \rangle \sim g(t/T)$. In order to obtain each collapsed pulse shape, two to ten earthquakes were averaged for each

value of T . In our mean field theory, the universal scaling function is $g_{mf}(x) = Ax(1 - x)$ with $x = t/T$. We plot this functional form (*bold curve*) with $A = 80$. Note the apparent asymmetry to the left in the observed data while the theoretical curve is symmetrical around its maximum. *Inset*: The raw data and the averaged data (before collapsed) (From Mehta et al. (2006))



Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems, Fig. 9 A collapse of averaged earthquake pulse shapes, $\langle dm_0(t|M_0)/dt \rangle$, with the size of the moment M_0 in Newton meters within 10 % of each size given in the legend, respectively. In order to obtain each collapsed moment rate shape, five to ten earthquakes were averaged for each value of M_0 . The collapse

$M\langle dm/dt \rangle(M, t)$, both for observations and the BZR model prediction. As shown in Mehta et al. (2006) and Sethna et al. (2001), the theory predicts

$$\langle dm/dt \rangle(M, t) \sim M^{1/2} q\left(t/M^{1/2}\right) \quad (15)$$

where the universal scaling function $q(x) = Ax \exp - Bx^2/2$ and the universal exponents are obtained from the mean field theory for the BZR earthquake model. A comparison between prediction and observational results for this scaling function is shown in Fig. 9.

Clearly, more data, especially for small earthquakes, are needed to decrease the statistical error bars of the observational data and determine the degree of agreement between theory and observations. An alternative scaling approach to moment rate data was given by Houston (2001) and a comparison between both approaches is discussed in Mehta et al. (2006).

Non-monotonic Models

We first consider including weakening of the cell failure threshold by an amount ϵ for sections which have already slipped in a given quake.

was obtained using the mean field scaling relation (Fisher et al. 1997): $\langle dm_0(t|M_0)/dt \rangle / M_0^{1/2} \sim f(t/M_0^{1/2})$. In our mean field theory, the universal scaling function is $f_{mf}(x) = Ax \exp - Bx^2/2$ where $x = t/M_0^{1/2}$. We plot this functional form (bold curve) with $A = 4$ and $B = 4.9$. Inset: The raw data and the averaged data (before collapsed) see Mehta et al. (2006))

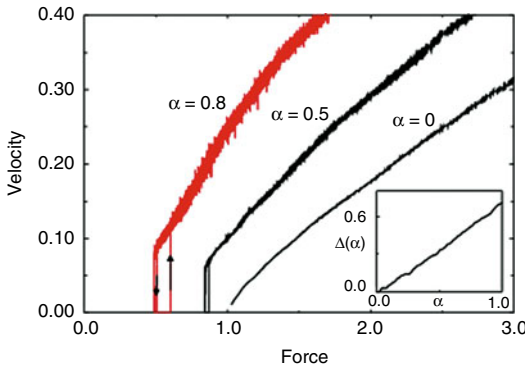
This crudely models the difference in static versus dynamic friction (see section “Models,” Eq. 5). In between quakes, all thus weakened thresholds heal back to their static strength. The effects of small weakening can be analyzed perturbatively.

With $\epsilon = 0$, consider a quake of diameter R_1 ($\ll L$ or ξ), with moment M_1 and area A_1 : i.e., A_1 sites have slipped. If a small ϵ is turned on at the end of the quake, all slipped sites that are within ϵ of slipping will now slip again – this will be $N_2 \sim \epsilon A_1$ sites. The simplest justifiable guess is that each of these will cause an approximately independent secondary quake. The total moment of these secondary quakes will be dominated by the largest one, so the extra moment will be $M_2 \sim (\epsilon A_1)$. (For a very large or infinite fault, this is obtained from $1 = N_2^{\text{ex}} \int_{M_2^{\text{ex}}}^{\infty} P(M) dM$ and inserting Eq. 10.) If $M_2^{\text{ex}} \ll M_1$, this process can continue but will not increase the total moment substantially. If $M_2^{\text{ex}} \sim M_1$, however, the process can continue with a larger area A_2 and hence a larger M^{ex} , leading to a catastrophic runaway event. From the above exponent relations and scaling laws, we obtain $B = 1/2$ and $A \sim M$, so that

for any ϵ , for large enough M_1 , $M_1 > M_D \sim \epsilon^{-2}$, M_2^{ex} will be comparable to M_1 and the quake will become much larger (runaway). In the force-driven infinite system for $F < F_c$, quakes of size ξ will runaway and become infinite if $\xi > \epsilon^{-1}$. Since $\xi \sim (F - F_c)^{-\nu}$ and $1/\nu = 1$, this will occur for $F_c - F < C_w \epsilon$ with some constant C_w . This result is very intuitive and justifies a posteriori the assumptions leading to it: Since on slipping, the random pinning forces, f_R , in a region are reduced by order ϵ , the effective critical force F_c for continuous slip will have been reduced by order ϵ ; thus, if $F > F_c(\epsilon) = F_c - C_w \epsilon$, the mean velocity $\bar{v}$ will be nonzero. A similar effect can be caused by stress pulses associated with Eq. 6. By considering which of the sites in a long quake with $\alpha = 0$ can be caused to slip further by such stress pulses, one finds that runaway will occur for $M \geq M_D \sim \alpha^{-4}$ for the physical case (Fisher et al. 1997). This has been checked in $d = 1$ with $\Gamma = 1$ and $\gamma = 0$, finding the predicted reduced critical force $F_c(\alpha) \sim F_c - C_p \alpha^2$ as shown in Fig. 10 (Fisher et al. 1997). These 1-d simulations also reveal a hysteretic $\bar{v}(F)$ curve in finite systems. This is expected to also occur with the model with weakening discussed above. Related higher dimensional systems are

discussed in Ramanathan and Fisher (1998) and in Hillers et al. (2007).

We can now understand what should happen with either weakening or stress pulses in finite systems driven with a weak spring or with slowly moving boundaries. As the system is loaded, quakes of increasing size are observed. If the system is small enough that it cannot sustain quakes with $M > M_D(\epsilon, \alpha)$, i.e., even events within the power law scaling regime of the event size distribution, with $M \leq M_D(\epsilon, \alpha)$, are system spanning, then the behavior will not be much different from the monotonic case with $\epsilon = \alpha = 0$. In both cases, there is a power law event size distribution all the way to the largest events that are determined by the system size. This will occur if the dominant linear system size L is less than the maximum possible linear extent of an earthquake that does not become a runaway event: $L < R_D(\epsilon, \alpha) \sim M_D^{1/2} \sim \max(C_a/\alpha^2, C_e/\epsilon)$ with appropriate coefficients C_a, C_e , which will depend on the amount of randomness in the fault. On the other hand, if $L > R_D$, quakes of size of order R_D will runaway and most of the system will slip, stopping only when the load has decreased enough to make the loading forces less than the lower end of the hysteresis loop in $\bar{v}(F)$ (as in Fig. 10).



Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems, Fig. 10 Mean velocity versus force for one-dimensional system with a non-monotonic kernel $J(x, t) = \delta(t - x)/x^2 + \alpha \delta'(t - x)/x$ for $\alpha = 0.8, 0.5, 0$. A spring or boundary-loaded system will traverse the hysteresis loops in the direction indicated. *Inset:* the threshold force, $F_c^1(\alpha)$, on increasing the load; $\Delta_\alpha = [1 - F_c^1(\alpha)/F_c^1(\alpha = 0)]^{1/2}$ is plotted versus α (From Fisher et al. (1997))

Because of the tendency of regions that have already slipped to slip further and the consequent buildup of larger stresses near the boundaries of the slipped regions, large events in systems with dynamic weakening will be much more crack-like than in monotonic models, probably with $\Delta u \sim L$. Statistics of quakes with weakening, ϵ , reasonably large, but no stress, pulses ($\alpha = 0$) are shown in Fig. 4 and in Ben-Zion (1996), and Ben-Zion and Rice (1993, 1995); note the absence of quakes with intermediate moments. A typical large event in this case is shown in Fig. 5b; it appears to be crack-like.

In this section, we have shown that simple models of heterogeneous faults – with the dimensionality and long-range elastic interactions properly included – can give rise to either power law statistics of earthquake moments or a distribution of small events combined with characteristic system-size events. Which behavior – or

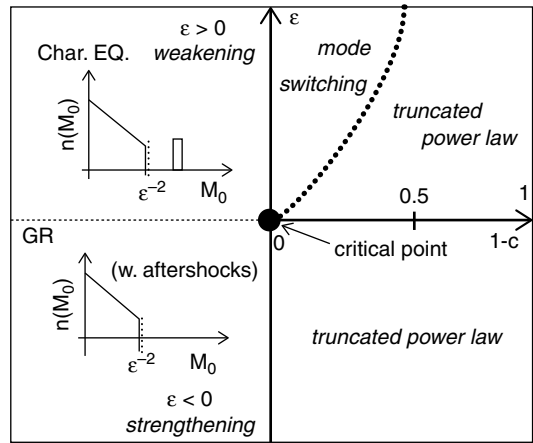
intermediate behavior – obtains is found to depend on a number of physical properties such as frictional weakening and dynamic stress transfer, analogs of which should definitely exist in real systems. In the power law regime, the conventionally defined Gutenberg-Richter exponent $b \equiv 3B/2$ (Ben-Zion 2003) is found to be $b = 3/4$. This is close to the observed b -value of global strike-slip earthquakes at depth less than 50 km (Frohlich and Davis 1993).

Mode Switching

In Dahmen et al. (1998), the mean field approximation of infinite range elastic interaction in the BZR model with $N = LW$ (with $W \sim L$) geometrically equal cells on the fault is used to write the local stress τ_i on cell i as

$$\begin{aligned} \tau_i &= J/N \sum_j (u_j - u_i) + K_L(vt - u_i) \\ &= J\bar{u} + K_L vt - (K_L + J)u_i, \end{aligned} \quad (16)$$

where u_i is the total fault offset of cell i in the horizontal (x) direction, $\bar{u} = \left(\sum_j u_j \right) / N$, J/N is the elastic coupling between cells in the mean field approximation, and K_L is the effective loading stiffness of the bulk material surrounding the fault patch. Instead of the loading spring stiffness K_L , a conservation parameter $c \equiv J/(K_L + J)$ is introduced, which equals the fraction of the stress drop of the failing cell, that is retained in the system after the slip. There, it is shown that for the physical loading spring stiffness $K_L \sim 1/L$, one has $1 - c \sim O(1/\sqrt{N})$. A value $c < 1$ for a large system would be physically realized if the external drive is closer to the fault than its linear extent. To be precise, mean field theory only gives the correct physical scaling behavior near the critical point at zero weakening $\epsilon \rightarrow 0$ and for $c \rightarrow 1$. In Dahmen et al. (1998), it is shown, however, that in a certain parameter regime for $\epsilon > 0$ and $0.5 < c < 1$ indicated in the phase diagram of Fig. 11, one finds a mode-switching behavior between Gutenberg-Richter statistics and characteristic earthquake statistics. Similar mode-switching behavior has also been seen in a more realistic three-dimensional model for



Physics of Jerky Motion in Slowly Driven Magnetic and Earthquake Fault Systems, Fig. 11 Phase diagram of the BZR model, described in the text. The range $\epsilon > 0$ represents dynamic weakening, while $\epsilon < 0$ represents strengthening. The parameter $1 - c$ quantifies the deviation from stress conservation in the mean field approximation of the model

coupled evolution of earthquakes and faults (Ben-Zion et al. 1999; Lyakhovsky et al. 2001) and in numerical simulations with the BZR model that includes elastic stress transfer (Zöller et al. 2004). In the mean field BZR model, the activity switching results from episodic global reorganization of the mode of strain energy release of the fault system, reflected in a “configurational entropy” of stress states on the fault (Dahmen et al. 1998). This is associated with a statistical competition between a tendency of a synchronized behavior leading to clusters of large earthquakes and the characteristic earthquake distribution and a tendency for disordered response leading to Gutenberg-Richter-type statistics without a preferred event size. Mode switching happens when these two opposite tendencies are roughly equal in strength. Some possible observational evidence for mode switching in earthquake data is discussed in Ben-Zion et al. (1999).

Results on Aftershocks

As mentioned in “Simple Models for Inhomogeneous Earthquake Faults,” we associate regions off the main fault segments that are in an early

deformation stage with dynamic strengthening $\epsilon < 0$. To capture basic aspects of brittle deformation on such regions in the three-dimensional volume around the main fault (Fig. 3), we change the model as follows: when any cell i slips during an earthquake and thereby reduces its stress by $\Delta\tau_i \equiv \tau_{f,i} - \tau_{a,i}$, the failure stress $\tau_{f,j}$ of every cell $j = 1, \dots, N$ is *strengthened* by an amount $|\epsilon|\Delta\tau_i/N$. Once the earthquake is complete, the failure stress of each cell is slowly lowered back to its original value. This represents in a simple way the brittle deformation that occurs during an earthquake in the off-fault regions, which are first in a strengthening regime, compared to the main fault, and then have a weakening process. The events that are triggered as the failure stresses are lowered in the weakening period are referred to as *aftershocks*. The occurrence of aftershocks in this version of the model for off-fault regions is in agreement with the observation that a large fraction of observed aftershocks typically occur in off-fault regions (Utsu et al. 1995). For this version of the model with $\epsilon < 0$, both the primary earthquakes (i.e., mainshocks) and the triggered aftershocks are distributed according to the Gutenberg-Richter distribution, up to a cutoff moment scaling as $1/\epsilon^2$. Assuming that the increased failure stress thresholds $\tau_{f,i}$ are slowly lowered with time as $\log(t)$ toward their earlier static values $\tau_{s,i}$ and that the stresses are distributed over a wide range of values, we show analytically in Mehta et al. (2006) that the temporal decay of aftershock rates at long times is proportional to $1/t$, as in the modified Omori law $\Delta N/\Delta t K/(t+c)^p$ with $p = 1$ (Ben-Zion 2003; Utsu 2002; Utsu et al. 1995), where N is the cumulative number of aftershocks, t is the time after the mainshock, and K , c , and p are empirical constants.

Remarkably, the long length-scale behavior of this model can be shown (Mehta 2005) to be the same as the behavior of the mean field BZR model given in Eq. 16 with an added “antiferroelastic” term $(-\epsilon|J\bar{u})$:

$$\tau_i = J\bar{u} + K_L v t - (K_L + J)u_i - |\epsilon|J\bar{u}. \quad (17)$$

In Eq. 17, every time a cell fails, it slips by an amount Δu_i that leads to stress loading of the other cells, lessened by $|\epsilon|J\Delta u_i/N$ compared to our original model (Eq. 16). On the other hand, in the global strengthening model (described above), when a cell slips, the failure stresses of all cells are strengthened by $|\epsilon|J\Delta u_i/N$. On long length scales, the global strengthening of the failure stress has equivalent effects on the earthquake statistics as the dissipation of the redistributed stress, up to corrections of order $O(1/N)$, so the scaling behavior for large events of both models are the same. Moreover, Eq. 17 can be rewritten as

$$\tau_i = J[1 - |\epsilon|][\bar{u} - u_i] + K_L v t - [K_L + J|\epsilon|]u_i. \quad (18)$$

We can now absorb $|\epsilon|$ by defining $J' = J(1 - |\epsilon|)$ and $K'_L = K_L + J|\epsilon|$. Rewriting Eq. 18 with the new definitions and dropping the $|\epsilon|$ contribution in $[K'_L - J|\epsilon|]v t$ since $v \rightarrow 0$, we find

$$\tau_i = J'\bar{u} + K'_L v t - (K'_L + J')u_i. \quad (19)$$

Therefore, we recover Eq. 16 with $J \rightarrow J'$ and $K_L \rightarrow K'_L$. This amounts to changing the stress conservation parameter c (from reference (Dahmen et al. 1998)). For Eq. 19

$$c = J'/(K'_L + J') = 1 - |\epsilon| \quad (20)$$

where $K_L \rightarrow 0$ since we are concerned with the adiabatic limit. We also know (from reference (Dahmen et al. 1998)) that the cutoff S_{cf} for the Gutenberg-Richter distribution scales as $S_{cf} \sim 1/(1-c)^2$. Thus, from Eq. 20, we find that the cutoff for Eq. 17 will scale as $\sim 1/|\epsilon|^2$.

Mapping to Single-Interface Magnet Model

The mean field version of the single-interface magnet model with infinite range antiferromagnetic interactions is given by (Durin and Zapperi 2001; Zapperi et al. 1998)

$$\dot{h}_i(t) = J[\bar{h} - h_i(t)] + H(t) - k\bar{h} + \eta_i(h) \quad (21)$$

where $h_i(t)$ is the position of the domain wall, $H(t)$ is the external driving field, k is the coefficient of the antiferromagnetic term, and $\eta_i(h)$ is the pinning field. In the paper by Fisher et al. (1997), it has been shown that the scaling behavior on long length scales resulting from Eq. 5, without the $-|\epsilon|J\bar{u}$ term, is the same as that of Eq. 21 without the antiferromagnetic term $-k\bar{h}$. Furthermore, upon inspection, we see the following correspondence between the single-interface magnet model (Eq. 21) and the mean field earthquake model (Eq. 17):

$$-k\bar{h} \Leftrightarrow -|\epsilon|J\bar{u} \quad (22)$$

In other words, the coefficient of the antiferromagnetic term k plays the same role in the magnet model (Eq. 21), as the coefficient of strengthening $|\epsilon|J$ does in the earthquake model (Eq. 17).

Summary

Phase Diagram

The regimes with various statistics produced by the model are summarized by the phase diagram given in Fig. 11. The range $\epsilon > 0$ corresponds to “mature” localized faults with a weakening rheology and characteristic earthquake statistics. The value $\epsilon = 0$ corresponds to “immature” strongly inhomogeneous fault zones and fault networks with power law statistics and scale-invariant rupture properties. The range $\epsilon < 0$ corresponds to the fracture and fault networks around large rupture zones, characterized by strengthening due to the creation of new structures and associated emerging aftershocks. The right side of the diagram summarizes the mean field theory results on mode switching described in “Mode Switching.” The left side of the phase diagram resembles the phase diagram for avalanches in the nucleation RFIM for magnets (Sethna et al. 1993). There, too, increasing the disorder from small to large (compared to the ferromagnetic coupling between the individual domains) drives the system from a characteristic avalanche size distribution to a

truncated power law, with a disorder-induced critical point separating the two regimes.

It may be surprising that the discussed simple BZR model can capture many of the essential general features of earthquake statistics (or other systems with avalanches, such as driven magnetic domain walls). This can be understood through the renormalization group (Binney et al. 1993; Sethna et al. 2001), a powerful mathematical tool to coarse grain a system and extract its effective behavior on long space-time scales. Many microscopic details of a system are averaged out under coarse graining, and universal aspects of the behavior on long scales depend only on a few basic properties such as symmetries, dimensions, range of interactions, weakening/strengthening, etc. When a model correctly captures those basic features, the results provide proper predictions for statistics, critical exponents, and universal scaling functions near the critical point. Consequently, many models that are in the same universality class lead to the same statistics and exponents (Binney et al. 1993; Dahmen et al. 1998; Fisher et al. 1997; Sethna et al. 2001).

Conclusions

The phenomenology of earthquakes and avalanches in magnets exhibits a number of power law distributions and scale-invariant functions (Table 1). In search of basic model ingredients that can explain these results, we have focused on models that are rich enough to produce a diversity of observed features, while being simple enough to allow analytic predictions on long spatiotemporal scales. For the earthquake system, we use the BZR model for a heterogeneous fault with threshold dynamics and long-range stress-transfer interactions (Ben-Zion 1996; Ben-Zion and Rice 1993, 1995). For the magnet system, we use variants of the RFIM model with threshold dynamics and both short-range and long-range interactions (Kuntz and Sethna 2000; Sethna et al. 1993, 2001; Zapperi et al. 1998). In both classes of models, changes in the property disorder and dynamic effects lead to different dynamic regimes (Fig. 11). For different ranges of parameters, the

earthquake model produces fractal and crack-like slip functions, power law frequency-size statistics, characteristic earthquake distribution, mode switching, and aftershocks. Similar features are found with the magnet models. We discussed two universal scaling functions of moment rates near criticality as a stronger test of the theory against observations than mere scaling exponents that have large error bars. As in magnetic systems, we find that our analysis for earthquakes provides a good overall agreement between theory and observations but with a potential discrepancy in one particular universal scaling function for mean moment-rate shapes at fixed duration. The discrepancy has an interesting precedent in the context of avalanches in magnetic systems and has been explained there in terms of nonuniversal time retardation effects due to eddy currents. Similar retardation effects may be due to triggering delays or strengthening effects that are responsible for aftershocks in earthquake faults. More observational data, in particular on small earthquakes, would be needed to test some of the predictions in detail.

Future Directions

We have highlighted some interesting connections between earthquake and magnet systems with a jerky response to a slowly varying driving force. Future useful studies include analysis of factors controlling nucleation processes, transitions to instabilities, and final event sizes, along with a more detailed analysis of the effects of geometrical heterogeneities in the fault structure on the statistics of earthquakes. Additional observational data, particularly for small earthquakes, are needed to test predictions for the scaling of the earthquake duration and rupture area with moment and for accurately testing our mean field predictions for moment rate shapes. Developing analytic corrections to the mean field earthquake models can provide additional important insights. Testing similar ideas in other systems with crackling noise would improve and deepen our understanding of universal behavior in disordered nonequilibrium systems.

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Flexible Mechanical Structures and Their Topologically Protected Deformations

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Article Outline

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Glossary

Bloch mode A mode of a periodic structure that differs between unit cells only by a phase factor, with the physical part understood to be the real part of the complex field.

Constraint Some algebraic, usually linear, equation relating a condition between degrees of freedom that must be satisfied. Violations of a linear constraint cost an energy proportional to the constraint's stiffness, and in the limit of infinite stiffness the constraint is called strict and is always satisfied. The most common type of constraint that one considers is that the distance between two particles not change.

Degree of Freedom A scalar number partially describing the configuration of a system. Most often, a component of a displacement of a particle from its initial position.

Dynamical Matrix A self-adjoint linear operator, typically denoted $\mathbf{D}$, that maps from the

vector of the system's degrees of freedom to the vector of the forces.

Equilibrium Matrix A linear operator, typically denoted $\mathbf{Q}$, whose i, j element describes the linear scaling between the tension associated with the violation of the j th constraint and the force on the i th degree of freedom. Its transpose is the rigidity matrix.

Floppy mode A deformation mode of a structure that satisfies all constraints to linear order and thus costs zero energy. That is, a zero mode that changes the shape rather than just the position or orientation of the structure.

Rigid A structure is rigid if the only way in which it can be continuously deformed is via the Euclidean motions of uniform translations and rotations of the whole structure.

Rigidity Matrix A linear operator, typically denoted $\mathbf{C}$ whose i, j element describes the linear scaling between the j th degree of freedom and the i th constraint. Its transpose is the equilibrium matrix.

Self stress A set of tensions within bonds that generates no net force on any particle or pseudo-force on any degree of freedom.

Stiffness Matrix A self-adjoint linear operator, typically denoted $\mathbf{K}$, that maps from the vector of the violations of the system's constraints to the vector of the associated tensions. In the case that all of the constraints consist of springs, the stiffness matrix is a diagonal matrix whose elements are the spring stiffnesses.

Topological Invariant Also called a topological number, this is a number, usually an integer or a binary number, that corresponds to a topological state and thus changes only via abrupt transitions.

Winding Number An integer topological invariant associated with a map from the one-sphere (a circle) to itself. This is the net number of times the mapped function covers the one-sphere each time one winds around the original space. It assumes different physical significance in different systems.

Zero Mode An infinitesimal deformation or Euclidean motion of a structure that satisfies all constraints to linear order and thus costs zero energy.

Introduction

The particles composing a fluid continuously rearrange themselves. In contrast, a solid object possesses bonds of sufficient strength such that the relative positions of its composite particles are fixed, up to overall rigid-body rotations and translations. In conventional equilibrium physics, phase transitions shift systems abruptly from solid to fluid, with no intermediate regime.

However, as permanent bonds (or the temporary contact forces present in, e.g., granular systems) are added to a structure one by one it acquires the ability to support external loads before it is reduced to a single rigid configuration. Such *flexible structures* are able to undergo prescribed motions and have tremendous utility in locomotion, manipulation, and shape-changing. Consequently, they are ubiquitous in both biology and in technological applications.

As will be explored here, such flexible objects realize complex algebraic structures. A rigid, solid object possesses only a single minimum-energy shape and the particles of a fluid explore an ensemble of nearly any possible set of positions, but the subset of spatial embeddings of a set of particles that satisfy a critical number of bond constraints can describe a complex, high-dimensional manifold. Remarkably, when the structure has long-range (typically periodic) order in its bulk, this can actually determine the existence of modes on the boundary, the *topological bulk-boundary correspondence* of flexible mechanical structures (Kane and Lubensky 2014). This same principle extends not only to purely geometrical embeddings but also to structural *dynamics* (Süsstrunk and Huber 2016).

Rigidity

Consider a set of point particles, each with no internal structure or orientational degrees of

freedom, with positions in D -dimensional space given by $\{\mathbf{r}_i\}$ and with some sets of bonds of rest lengths ℓ_α and some bond topology of the form $p_\alpha = (i, j)$ specifying that bond α connects particles i, j . One can then define the extension function,

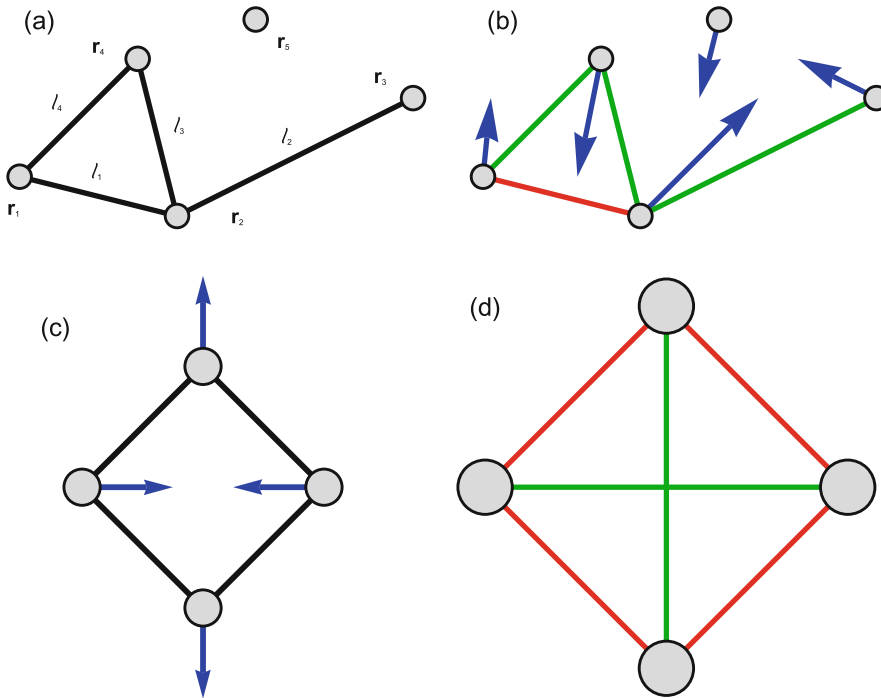
$$e_\alpha \equiv |\mathbf{r}_{p_{\alpha,2}} - \mathbf{r}_{p_{\alpha,1}}| - \ell_\alpha, \quad (1)$$

where a positive value indicates extension of the bond and a negative amount indicates compression.

A *rigid embedding* is then a set of particle positions that satisfies the *constraint equations* $e_\alpha = 0$. As will be explored below, different mechanical constraints may arise as well.

The space of embeddings of N_p particles in D -dimensional Cartesian space is simply the tensor product of N copies of $\mathbb{R}^D$. In the absence of any bonds, the space of rigid embeddings is this entire $N_p D$ -dimensional space. Including a single bond of finite length reduces the dimension of this space by one. For example, in three dimensions, once the position of one particle connected to the bond is fixed, the second must lie on a two-dimensional sphere centered on that particle rather than at an arbitrary point in three-dimensional space. In contrast, including a bond of vanishing length reduces the dimension of the space of rigid embeddings by D , since it requires each of the D components of the position of the second particle to coincide with the first. Unless otherwise stated, bonds will be taken to have finite rest length. This simple counting argument, in which a single constraint can reduce the space of allowed embeddings, goes back to JC Maxwell's foundational 1864 formulation of mechanical constraints (Maxwell 1864).

Continuing in this way, adding an additional bond reduces the manifold of rigid embeddings to a submanifold one dimension lower. However, two special cases present themselves. Consider as the first a rigid bond structure such that the distance between two particles is fixed. Placing a bond between these two particles with rest length equal to this distance will have no affect on the rigid states of the system. As a slightly more complicated example, consider the structure in Fig. 1d, in which four particles in two dimensions



Flexible Mechanical Structures and Their Topologically Protected Deformations, Fig. 1 (a) A system of particles (gray dots) located at positions $\mathbf{r}_i$ joined by bonds of lengths l_j , with the blackness of the bonds indicating that they are at their rest lengths. (b) Particles undergo displacements indicated by blue arrows that extend (red) or

compress (green) the bonds. Alternately, the same diagram could represent tensions within bonds and the external forces needed to balance them. (c) A set of displacements that does not stretch any bonds: a zero mode. (d) A set of tensions that does not generate a force on any particle: a state of self stress

are arranged in a square with bonds between each pair of particles. Either one of the two bonds that crosses the interior of the square suffices to render the structure rigid, meaning that the second such bond is redundant. Such *redundant bonds* allowed Maxwell to identify a necessary but not sufficient number of bonds to render a mechanical system with a certain number of degrees of freedom rigid. The simplest example of such a redundant bond would be one placed between two particles that are already bonded.

Alternately, one could take a pair of particles of fixed rigid separation and place a bond between them with some other rest length. Because this new, *incompatible* constraint cannot be satisfied simultaneously with the existing ones, this eliminates entirely the rigid embeddings. The result must be a *stressed* structure in which at least one constraint is violated. A trivial example would be

the joining of three particles via three bonds whose lengths do not satisfy the triangle inequality. Another example, returning again to Fig. 1d, would occur if one of the rest lengths of any of the bonds were changed, so that no embedding of the structure could achieve all of the rest lengths.

Linearization

Flexible structures possess fascinating and rich sets of nonlinear modes, from the shearing of the simple square truss of Fig. 1c to the folding of the most intricate origami. However, in order to make contact most directly with topological band theory, it is necessary for us to narrow our focus, at least temporarily, to infinitesimal deformations of structures about rigid embeddings. Consider an embedding subject to infinitesimal displacements such that $\mathbf{r}_i \rightarrow \mathbf{r}_i + \mathbf{u}_i$. Via Eq. (1), the extension of a bond between particles i, j is

$$e_\alpha = |\mathbf{r}_j - \mathbf{r}_i + \mathbf{u}_j - \mathbf{u}_i| - \ell_\alpha \quad (2)$$

$$\begin{aligned} &= |\mathbf{r}_{ij}| - \ell_\alpha + \hat{\mathbf{r}}_{ij} \cdot \mathbf{u}_{ij} \\ &+ \frac{1}{2|\mathbf{r}_{ij}|} \left[\mathbf{u}_{ij}^2 - (\hat{\mathbf{r}}_{ij} \cdot \mathbf{u}_{ij})^2 \right] \\ &+ O(u^3), \end{aligned} \quad (3)$$

where $\mathbf{v}_{ij} \equiv \mathbf{v}_j - \mathbf{v}_i$, $\hat{\mathbf{v}} \equiv \mathbf{v} / |\mathbf{v}|$. For a rigid embedding, $|\mathbf{r}_{ij}| - \ell_\alpha = 0$ and consequently the linear extension takes the simple form:

$$e_\alpha = \hat{\mathbf{r}}_{ij} \cdot \mathbf{u}_{ij}. \quad (4)$$

We may then describe the linear relationship between the vector of extensions $\mathbf{e}$ and the vector describing the displacements of all the particles, $\mathbf{u} \equiv (\mathbf{u}_1, \mathbf{u}_2, \dots, \mathbf{u}_{N_p})$ (here denoting a concatenation of vectors into a vector, not composition into a matrix) via the linear map

$$\mathbf{e} = \mathbf{C}\mathbf{u}, \quad (5)$$

where $\mathbf{C}$ is known as the compatibility matrix, or sometimes the rigidity matrix, since its nullspace is the set of deformations that are rigidly compatible with one another. Such modes, costing zero energy and resulting in zero extension (to linear order) are referred to as *zero modes*.

We now introduce minimal dynamics by supposing that our bonds generate a Hookean return force. In this case, the system's potential energy takes the form

$$E = \frac{1}{2} \mathbf{e}^T \mathbf{K} \mathbf{e}, \quad (6)$$

where $\mathbf{K}$ is a diagonal matrix with each element k_α the spring constant associated with bond α . From this, one may obtain the vector of forces $\mathbf{f}$ that the structure exerts on all the degrees of freedom:

$$\mathbf{f} = -\nabla_{\mathbf{u}} E = -\mathbf{C}^T \mathbf{K} \mathbf{C} \mathbf{u}. \quad (7)$$

In terms of the vector of tensions $\mathbf{t} = \mathbf{K} \mathbf{e}$ and defining the *equilibrium matrix* $\mathbf{Q} \equiv \mathbf{C}^T$ this becomes

$$\mathbf{f} = -\mathbf{Q} \mathbf{t}. \quad (8)$$

Note that the minus sign is not always present in the literature as $\mathbf{f}$ can be defined as the external force that must be applied in equilibrium to overcome internal forces. Just as the nullspace of the compatibility matrix gives the compatible displacements, the nullspace of the equilibrium matrix gives the sets of tensions that result in no net force. Collectively, the configurations without any tensions and those in which tension forces are balanced are known as *equilibrium configurations*. A set of tensions in the latter is known as a *state of self stress*.

The linear representation above gives for a single vertex i :

$$\mathbf{f}_i = -\sum_{\alpha} t_{\alpha} \hat{\mathbf{r}}_{\alpha}, \quad (9)$$

where α is summed over all edges connected to vertex i and $\hat{\mathbf{r}}_{\alpha}$ is the unit vector along edge α pointing away from this vertex.

Although Maxwell was not able to identify redundant bonds systematically, this formulation allowed Calladine, over a century later (Calladine 1978), to derive a relationship between zero modes and states of self stress. Let N_{dof} , N_{con} , N_{ZM} , N_{SS} refer, respectively, to the numbers of degrees of freedom, constraints, zero modes, and states of self stress. In linear algebra, the rank of a matrix is defined as dimension the space spanned by its columns. Deformation modes spanned by $\mathbf{C}$'s columns are the complement of modes in its nullspace and tensions spanned by the columns of $\mathbf{Q}$ are the complement of its nullspace. Hence,

$$\text{rank}(\mathbf{C}) + N_{\text{ZM}} = N_{\text{dof}}, \quad (10)$$

$$\text{rank}(\mathbf{Q}) + N_{\text{SS}} = N_{\text{con}}. \quad (11)$$

However, using the well-known linear-algebraic result that column and row ranks are equal, $\mathbf{Q} = \mathbf{C}^T$ implies $\text{rank}(\mathbf{C}) = \text{rank}(\mathbf{Q})$, leading to the *Maxwell-Calladine index theorem*:

$$N_{\text{ZM}} - N_{\text{SS}} = N_{\text{dof}} - N_{\text{con}}. \quad (12)$$

Thus, one may see that each additional constraint *either* eliminates a zero mode or generates a state

of self stress. Similarly, each additional degree of freedom either generates a zero mode or eliminates a state of self stress. Zero modes and self stresses are subtly related to one another, composing the right and left nullspaces of a linear operator that connects two distinct vector spaces. Although it is not in general possible to derive one from the other, this result demonstrates that the two are related. This is particularly evident in *Maxwell* or *mechanically critical* systems, defined as those for which $N_{\text{ZM}} = N_{\text{SS}}$. In this case, zero modes and states of self stress are equal to one another in number (Fig. 2).

Periodic Structures

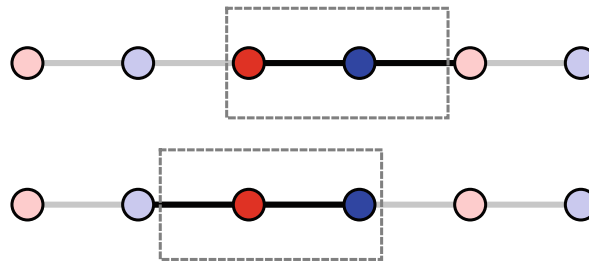
As is well-known in condensed matter physics, systems with discrete periodic structure crystals have significantly different properties than either isolated atoms or amorphous structures. This is because, per Bloch's theorem as discussed below, the normal modes of the system become grouped into smooth, analytically tractable bands. However, the consequences of periodicity are even more profound in rigidity theory as periodic structure can not only group zero modes but, due to redundancy, generate them.

Consequently, one may consider a system with periodic structure, with a cell indexed by $\mathbf{n} = (n_1, n_2, \dots, n_{D_c})$. Note that the number of lattice directions D_c may be less than the dimension of the space, as in the case of chains and sheets (e.g.,

origami) that have only one or two discrete translational symmetries despite being embedded in three dimensions. Thus, the spatial embedding of one of the n_p particles per cell indexed by i is $\mathbf{b}_i + n_j \mathbf{l}_j$, where $\mathbf{b}_i$ are the basis vectors, $\mathbf{l}_j$ are the lattice primitive vectors and the repeated indices imply a sum.

The topology of the n_{con} bonds per unit cell must then be generalized to $p_\alpha = (i, j, \mathbf{n}_i, \mathbf{n}_j)$, where $\mathbf{n}_i, \mathbf{n}_j$ describe the cell indices of the particles relative to the bond. For example, bond one could connect particle one to particle 2 within the same cell, but bond two might connect particle two to particle one in the cell to its right. In that case, one could either choose to define this second bond to lie on the right-hand side of the first cell, $p_2 = (2, 1, 0, 1)$ or the left-hand side of the second cell, $p_2 = (2, 1, -1, 0)$. So long as these choices are made consistently they will remain valid and consequently they can be thought of as a sort of *gauge choice*. However, due to the discrete nature of this gauge, it does not have a conventional connection to a conserved current.

With this formulation one has an opportunity to represent two types of mode more efficiently in the periodic structure than in a general one. The first is Guest Hutchinson (GH) modes (Guest and Hutchinson 2003). One wishes to explore whether there is an infinitesimal rigid mode that consists of a uniform strain between cells



Flexible Mechanical Structures and Their Topologically Protected Deformations, Fig. 2 Here, one sees two representations of a periodic structure consisting of red particles at points $\mathbf{b}_1 + n\mathbf{l}_1$ and blue particles at points $\mathbf{b}_2 + n\mathbf{l}_1$. One sees two separate choices of unit cells, as indicated by the dashed boxes and darker colors. In both cases, the same pair of particles is chosen for the main unit cell but in the first case the bond that has a blue particle to its left and the

red particle to its right is chosen to lie on the right of the unit cell, whereas in the second case it is chosen to lie on the left of the unit cell. Using the notation in the main text, in which p_α is a list of the basis indices and lattice indices of the two particles connected via the bond, one has in either case $p_1 = (1, 2, 0, 0)$ for the bond with the red particle on its left. For the second bond, the two cases correspond, respectively, to $p_2 = (2, 1, 0, 1)$, $p_2 = (2, 1, -1, 0)$

coupled to identical rearrangements within those cells. Such rearrangements can be described as infinitesimal shifts δ_i^b, δ_k^l in the basis and lattice vectors. The resulting extension of bond α as indexed above is

$$e_\alpha = \hat{r}_{ij} \cdot (\delta_j^b - \delta_i^b + n_k \delta_k^l). \quad (13)$$

Note the resemblance between Eq. (13) and Eq. (4). Consequently one may term the map between changes to the crystal structure and bond extensions the *augmented compatibility matrix*. Repeating the Maxwell-Calladine logic above, one finds then that there are a number of linear deformations of the crystal at least equal to the number of ways to deform it less the number of constraints: $D(n_p + D_c) - n_{\text{con}}$. However, these include D uniform translations and $D(D - 1)/2$ rotations, the latter of which require simultaneous rotation of both basis and lattice vectors. Thus, one has Guest-Hutchinson type deformation modes of number

$$n_{\text{GM}} \geq D(n_p + D_c) - n_{\text{con}} - D(D + 1)/2. \quad (14)$$

Of particular importance is the case of periodic *Maxwell lattices*, which one defines as those with equal numbers of bulk constraints and degrees of freedom, $Dn_p = N_{\text{con}}$. In particular, for $D = D_c = 2$ there are four quantities that determine the lattice vectors (two components of two vectors) but only two translations and one rotation. Hence, one has a single Guest mode in 2D. In 3D, $D = D_c = 3$, there are instead three such modes. Consequently, Maxwell lattices do not have unique ground states but instead have a continuum of rigid periodic embeddings.

The simplest case is the two-dimensional simple square lattice, of Fig. 3a. This has one particle with coordination number four, and hence two bonds per cell. The lattice is thus defined by six numbers: the two components each of the basis vector of the single particle and the two lattice vectors. Even after satisfying the two constraints, this leaves us with a four-dimensional space of

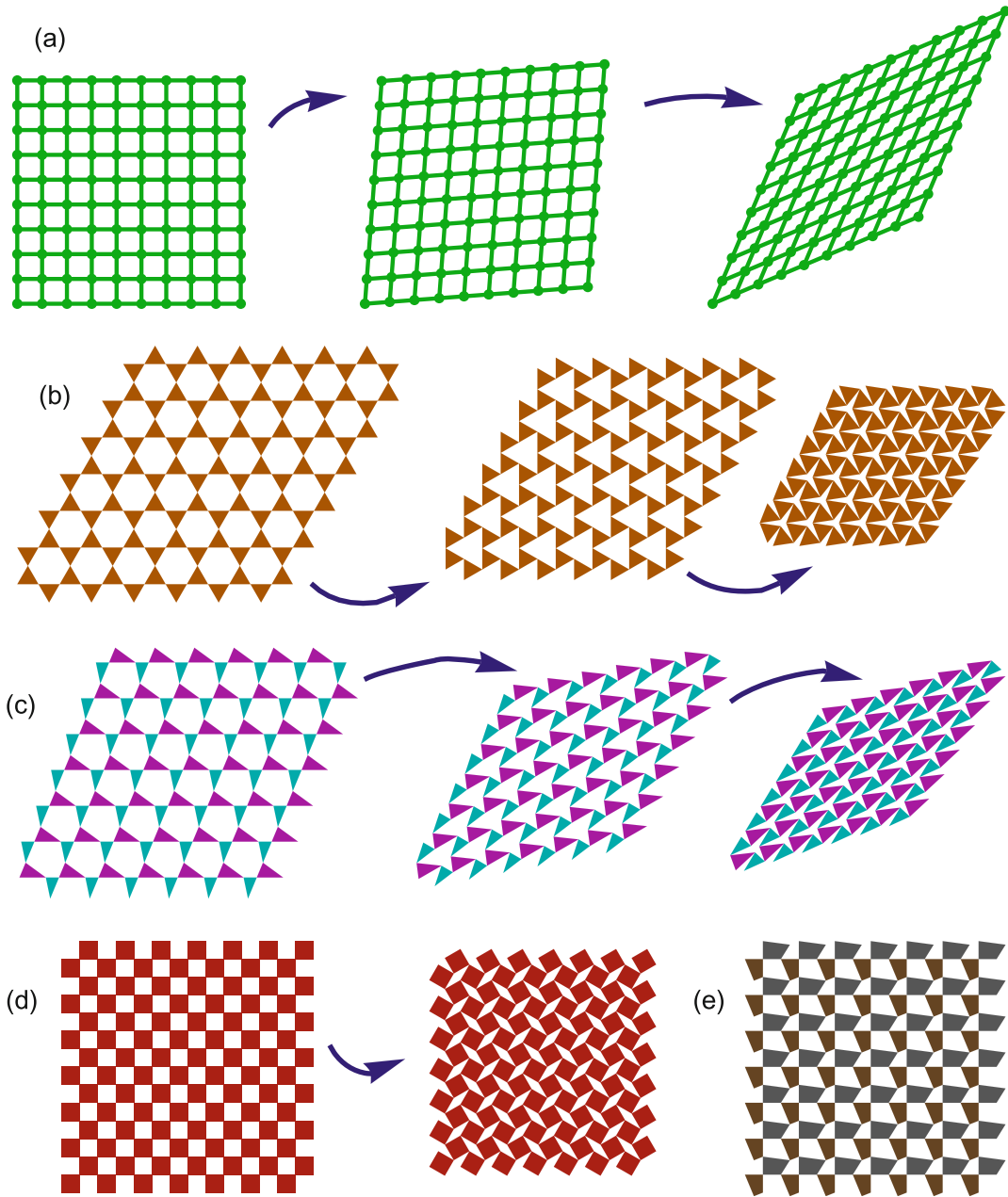
rigid periodic embeddings, only three dimensions of which are satisfied by the rigid-body rotations (two translations and a rotation) in three dimensions. The remaining one-dimensional set of states is given by the GH mode, a shearing of the two bonds against one another.

The other commonly considered Maxwell lattice, one with a nontrivial basis, is the kagome of Fig. 3b. This consists of two rigid triangular pieces joined by edges. Thinking of the basis as three triangular vertices and the six constraints as the requirements that the distances between vertices on the same triangle must remain fixed, one sees that the Maxwell condition that $n_{\text{dof}} = n_{\text{con}}$ is met. Alternately, if one thinks of the basis as consisting of the positions and orientations of the two triangular pieces per cell, one again has six degrees of freedom. In this picture, the six constraints are the three places where the triangles touch remain in contact. Either way, the lattice possesses threefold rotational symmetry which would be broken by a shearing motion: hence, the GH mode is purely dilational. For the deformed kagome of Fig. 3c the counting argument holds but the symmetry is broken, so the GH mode mixes shear and dilation in a way that varies along the action of the mode. This is in contrast with a system of corner-sharing quadrilaterals that necessarily exists above the Maxwell point: there, the fourfold symmetry of Fig. 3d does permit a dilational mode, but when this symmetry is broken the system is generically rigid, as in Fig. 3e.

These GH modes are the sole rigid modes of Maxwell lattices that preserve their symmetry. However, the Maxwell counting argument indicates that in a finite system with open boundary conditions (i.e., missing constraints at the edges) there should emerge a number of zero modes proportional to the boundary of the system. As will be examined in the next section, this leads to a broader class of modes that do not preserve periodicity.

Spatially Varying Modes

The striking behavior of crystalline systems follows largely from Bloch's theorem, which states that in a periodic system governed by the



Flexible Mechanical Structures and Their Topologically Protected Deformations, Fig. 3

(a) The simple square lattice is a two-dimensional Maxwell lattice that therefore possesses a nonlinear Guest-Hutchinson (GH) mode that preserves the periodicity of its structure without stretching either of the two bonds per cell. The structure is defined by a basis vector and two lattice vectors, a six-dimensional space that can satisfy the two constraints and undergo three transformations: two translations, a rotation and the Guest mode. (b) The regular

kagome lattice similarly exists at the Maxwell point and possesses a GH mode; in this case the lattice's threefold rotational symmetry forbids shear and yields a purely dilational mode. (c) However, an irregular kagome lattice still possesses a GH mode, and the lack of symmetry merely means that the mode mixes shear and dilation. In contrast, corner-sharing quadrilaterals exist above the Maxwell point and consequently while the symmetric structure in (d) possesses a similar dilational mode, the irregular structure in (e) is rigid

Schrödinger equation the eigenstates of the fully periodic system differ between cells only by a phase factor. To develop this in the context of rigid frames, a broader class of deformations will be considered. Let $\mathbf{u}(\mathbf{n})$ describe the combined vector of n_p D -dimensional displacement vectors within cell $\mathbf{n}$. Then, consider a mode of the *generalized Bloch form*

$$\mathbf{u}(\mathbf{n}) = \begin{pmatrix} z_1^{n_1} & z_2^{n_2} & \dots & z_{D_c}^{n_{D_c}} \end{pmatrix} \mathbf{u} \equiv \mathbf{z}^{\mathbf{n}} \mathbf{u}. \quad (15)$$

That is, if $z_1 = r_1 e^{i\theta_1}$ then the mode is scaled by r_1 in magnitude and its phase is shifted by θ_1 as one shifts by one cell in the first lattice direction. Here one adopts the common convention that only the real part of the mode is physical, and $\mathbf{u}$ itself can contain both a real and imaginary component. Such a mode is then an eigenmode of the crystal translation operator in the i th direction with eigenvalue z_i .

In the standard Bloch argument, one would choose z_i to be phase factors and diagonalize the matrix (in this case, the compatibility matrix) to show that its eigenmodes, including zero modes, would take this form. However, this argument is complicated by the over-completeness of our basis. For now, let us calculate the extension of bond α in cell $\mathbf{n}$ with bond topology $p_\alpha = (i, j, \mathbf{n}_i, \mathbf{n}_j)$:

$$e_\alpha(\mathbf{n}) = \hat{\mathbf{r}}_{ij} \cdot [\mathbf{u}_j \mathbf{z}^{\mathbf{n}+\mathbf{n}_j} - \mathbf{u}_i \mathbf{z}^{\mathbf{n}+\mathbf{n}_i}] \quad (16)$$

$$= \mathbf{z}^{\mathbf{n}} \hat{\mathbf{r}}_{ij} \cdot [\mathbf{u}_j \mathbf{z}^{\mathbf{n}_j} - \mathbf{u}_i \mathbf{z}^{\mathbf{n}_i}]. \quad (17)$$

$$\mathbf{r}_{ij} = n_j \mathbf{l}_j + \mathbf{b}_j - (n_i \mathbf{l}_i + \mathbf{b}_i) \quad (18)$$

We then find that $\mathbf{e}(\mathbf{n})$ takes the form $\mathbf{e} \mathbf{z}^{\mathbf{n}}$ with

$$\mathbf{e} = \mathbf{C}(\mathbf{z}) \mathbf{u}. \quad (19)$$

This means that the compatibility matrix, and hence the equilibrium matrix, are Laurent polynomials in the complex variables z_i . From the form of Eq. (18) it is clear that generalized Bloch modes then possess a great advantage over other modes in satisfying the compatibility conditions. Since the extensions in different cells are simply rescaled, then a generalized Bloch mode that

obeys the constraints in one cell obeys them in all cells. In contrast, a mode that could not be represented as a linear combination of such modes would face non-redundant constraints across the whole periodic system and would not be expected to satisfy them all. The one exception is modes whose displacements grow linearly, as in the Guest-Hutchinson modes above, since the relative displacements then are constant, which is the special case $\mathbf{z} = 1$.

The nature of this quantity $\mathbf{z}$ determines the spatial extent of a mode. Consider for simplicity a one-dimensional system. If $z = e^{i\theta}$, then the mode varies periodically without growing or shrinking on average—it is a bulk mode. If $|z| < 1$, then the mode grows exponentially smaller (in addition perhaps to oscillatory behavior) as one moves rightward and consequently one would label it a left edge mode, since it is exponentially suppressed away from the left edge. Similarly, $|z| > 1$ implies a right edge mode. Since z could potentially lie anywhere within the complex plane, one has then a two-dimensional space of modes with the unit circle representing bulk modes, the unit disk representing left-edge modes and the rest of the plane the right edge modes (this picture becomes more symmetrical under stereographic projection, for which the two edges become the two hemispheres of the unit sphere). Thus, although bulk modes occupy the majority of the one-dimensional system, they are only a vanishing portion of the entire two-dimensional space of possible modes. More precisely, one might refer to such modes as possible edge modes, since it has not yet been specified which of them satisfy which boundary conditions—for example a zero mode would not generally be possible under fixed boundary conditions, nor a state of self stress under free boundary conditions. However, a rigid mode must satisfy this bulk condition, so a particular system's actual rigid modes will be a subset of those discussed here.

For reasons analogous to the above analysis, one would expect states of self stress to take on this same spatial variation pattern, with tensions rescaling and varying by phase factors across the cells. Repeating the above analysis then yields

forces and tensions related via a linear relationship of the form

$$\mathbf{f} = -\mathbf{Q}(\mathbf{z})\mathbf{t}. \quad (20)$$

Here, however, a subtlety emerges. If a bond is connected to a site in the positive first lattice direction, the displacement is rescaled relative to the extension by z_1 . However, this means the site is connected to a bond in the *negative* first lattice direction and consequently the tension is rescaled by $1/z_1$ relative to the force. Thus, one now has:

$$\mathbf{Q}(\mathbf{z}) = \mathbf{C}^T(1/\mathbf{z}). \quad (21)$$

That is, where a factor of z_i appears in the compatibility matrix, a factor of $1/z_i$ appears in the equilibrium matrix. Note that $z_i = 0$ is no more permitted than $z_i = \infty$, since either case would imply that a lattice translation would yield a diverging amplitude.

In a system that is not just periodic in the bulk but has periodic boundary conditions, the reciprocal-space rigidity and equilibrium matrices may be obtained by a discrete Fourier transform. For example, if the system repeats after N_i cells in the i th lattice direction, then the compatibility matrix can be expressed entirely as connections between displacement vectors at wavevectors of the form $z_i = \exp(in_i/(2\pi N_i))$ and extension vectors at the corresponding wavevector.

However, as the above real-space analysis shows, the result is much more general. Repeating the linear-algebraic analysis now yields

$$n_{\text{ZM}}(\mathbf{z}) - n_{\text{SS}}(1/\mathbf{z}) = n_{\text{dof}} - n_{\text{con}}. \quad (22)$$

In particular, for a Maxwell lattice with $n_{\text{dof}} - n_{\text{con}} = 0$ (the number of degrees of freedom per unit cell is related to the number of particles via $n_{\text{dof}} = n_p D$) one may say that for each zero mode on the left edge (with $|z_i| < 1$) there is exactly one state of self stress on the right edge (with $|z_i| > 1$). Referring to these two families collectively as force-balancing modes, it may be said that there are equal numbers of force-balancing modes on opposing sides of the lattice. This raises a question as to whether either type of mode by itself must be

divided evenly between the two edges in this way. This question is of fundamental importance to the topic of topological rigid modes.

Topological Boundary Modes of Maxwell Lattices

Consider a Maxwell lattice whose rigid modes are then governed by a square matrix, $\mathbf{C}(\mathbf{z})$, where for simplicity a single direction of crystal periodicity is considered. If a rigid mode $\mathbf{u}$ exists at some z such that $\mathbf{C}(\mathbf{z})\mathbf{u} = 0$, it follows that $d(\mathbf{z}) \equiv \det[\mathbf{C}(\mathbf{z})] = 0$. Hence, the spatial extent of zero modes may be found simply by finding the zeros of the determinant function $d(\mathbf{z})$. From Eq. (18) it follows that this is a finite Laurent polynomial. One may rescale this polynomial by some integer power of z through the appropriate choice of gauge (i.e., choosing whether one labels bonds as appearing on the right- or left-hand side of the crystal cell), as shown in Fig. 2. The *minimal gauge*, in which the lowest power of z in the polynomial is a constant, is chosen. In this gauge, each bond that connects two adjacent cells contributes a power of z (and a bond that connects cells shifted relative to one another by n contributes a power of z^n). Recall that the Fundamental Theorem of Algebra states that the total number of zeros of a polynomial in the complex plane, counting multiplicity, is the degree of the polynomial. Hence, the total number of zeros is the number of intercell constraints weighted by the difference in cell index between the particles at the two ends of the bond. In the common case in which intercell bonds connect only adjacent cells, this is simply the number of intercell bonds per cell, making sure not to count a bond twice because it connects two cells.

While ample numerical methods exist to solve for each of these modes, deep analytical insight may be obtained by instead attempting to count the total number of modes that lie on one edge. The left edge is chosen, since $|z| < 1$ is compact. The number on the right edge may be obtained either by using the Fundamental Theorem of Algebra or by using the transformation $z \leftrightarrow 1/z$ to exchange the two regions.

First, note that $d(z)$, as an analytic function, has a phase that is well-defined everywhere in the plane up to multiples of 2π . Indeed, as one winds around a single zero the phase winds by the degree (multiplicity) of the zero, and the phase does not wind at all in a region that contains no zeros (the polynomials do not contain branch cuts and the choice of gauge prevents poles). Consequently, the number of times the phase increases by 2π around a loop in the complex plane is simply the number of zero modes contained by the loop (counting multiplicity). In particular, if one chooses a contour running counterclockwise around the unit circle, one finds that the number of zero modes on the left edge is

$$\begin{aligned} N_L &= \frac{1}{2\pi i} \int_{-\pi}^{\pi} dq \partial_q \log \det \mathbf{C}(e^{iq}) \\ &= \frac{1}{2\pi i} \oint dz \partial_z \log d(z). \end{aligned} \quad (23)$$

Here the fact that the imaginary part of the logarithm a complex number is its argument is used. The final integral is performed in the positive (counterclockwise) direction around the unit circle in the complex plane.

The quantity N_L is a *topological number*. Topological quantities are those that remain unchanged under classes of deformations of the underlying system. Perhaps most famously, the Gauss-Bonnet theorem shows that the genus (number of holes) of a closed two-dimensional surface embedded in three dimensions can be obtained from the integral of its Gaussian curvature over that surface and hence this integral remains unchanged under deformations that do not pierce the surface. Other real-space topological quantities include knot invariants, the charges of liquid-crystalline topological defects and the Burgers vectors describing crystal topological defects. However, as will be seen, Eq. (23) most closely resembles the invariants of *topological insulators* (Hasan and Kane 2010), electronic systems with periodic structure whose bulk invariants protect surface conducting states.

In the same way, Eq. (23) describes a mechanical topological insulator. The zero modes can “conduct” displacements by generating them at

zero energy. The invariant cannot be changed without a zero passing from inside the unit disk of mode space in the complex plane to outside it, which necessarily implies that the zero modes enter the bulk bands, breaking the bulk mechanical insulator. Thus, the number of zero modes on a surface is protected by the insulating character of the bulk. This type of relationship between the number of modes on a boundary and a bulk topological invariant is referred to as *bulk-boundary correspondence*.

The winding number is in fact a special case of a type of topological invariant known as a *homotopy* group. Topologically, the Brillouin Zone of the bulk bands is equivalent to a circle, or the one-sphere, S^1 , since the dimensionless wavevector q is invariant under increases of 2π and points on the one-sphere are similarly invariant under an increase in phase of 2π . Similarly, the phase of $d(z)$ lies on S^1 . Consequently, the winding number is the first homotopy group of S^1 , $\pi_1(S^1) = \mathbb{Z}$ and indeed the winding number can take on any integer value.

Topological Invariants in Higher Dimensions

Although the topological invariant is, as derived in the previous section, a one-dimensional invariant, it nevertheless has implications for structures that are periodic in two or three spatial dimensions. One may define the winding number in the i th direction as

$$N_i(\{q_{-i}\}) = -\frac{i}{2\pi} \int_{-\pi}^{\pi} dq_i \partial_{q_i} \log \det \mathbf{C}(e^{iq}). \quad (24)$$

As before, this must comprise an integer invariant. However, the rigidity matrix is a function of the entire wavevector, and consequently the number of zero modes on the surface of the system from which q_i counts up from is in general a function of the other components of the wavevector, $\{q_{-i}\}$.

In the deformed kagome lattices first considered by Kane and Lubensky (2014), the winding numbers are independent of these transverse momenta. However, in other lattices, including the deformed square lattice, these invariants do

indeed vary at different wavevectors. As is required of an integer topological invariant, they shift abruptly by integer amounts. This implies the existence of a zero mode at some real wavevector within the Brillouin Zone, a *Weyl point* (Rocklin et al. 2016). This Weyl point is itself topologically protected, in that the winding of $\det \mathbf{C}$ is nonzero around it. For a simple Weyl point, the bulk winding number shifts by one across it, and hence the winding number around the Weyl point is ± 1 .

Because the rigidity matrix is a polynomial of e^{iq} with real coefficients, it follows that within the Brillouin zone (though not for edge modes) $\det \mathbf{C}(-\mathbf{q}) = [\det \mathbf{C}(\mathbf{q})]^*$. Thus, if there is a Weyl point at $\mathbf{q}$, such that the determinant vanishes there, there is another Weyl point at $-\mathbf{q}$ with the opposite winding number. Such winding numbers are preserved under deformations of the lattice, so individual Weyl points cannot spontaneously be created or destroyed. However, they can be removed when two with opposite charge come into contact, as is the case at high symmetry points where $q_i = -q_i \bmod 2\pi$. That is, at $q_i = 0, \pi$.

The topological invariant of Eq. (23) is a fundamentally one-dimensional quantity. It is perhaps surprising, then, that it leads to directly observable behavior in higher-dimensional systems. Nevertheless, the dependence on the transverse wavevector highlights that in higher dimensions this is not a simple, global topological invariant. This motivates us to ask whether such invariants do exist. To address this, one must think more carefully about the structure of degrees of freedom and constraints, as they exist for linear modes of periodic cells. A mode is defined by the complex z_i which describe how it oscillates and grows between cells, and by the complex u_i that describe its structure within the cell. More precisely, $\mathbf{u}$ can be treated as living in a complex projective space (in which two complex vectors are considered the same if they are the same up to an overall scale and phase, $\mathbf{u}_1 = \lambda e^{i\phi} \mathbf{u}_2$). Hence, the space of all possible z -periodic modes is

$$2(n_{\text{dof}} - 1 + D_c), \quad (25)$$

where the factor of two reflects the real and imaginary components of complex numbers. The term

n_{dof} is for the mode's internal cellular degrees of freedom, D_c is for the complex wavevectors that describe how the mode varies between cells and the -1 is because modes are equivalent under complex projection. Each additional complex constraint imposes two algebraic equations that a zero mode must satisfy. Suppose also that rather than varying exactly one z_i and holding the others fixed as done previously, let us allow $n \leq D_c$ of the z_i to vary. Therefore, isolated zero modes such as the ones thus far considered would require a balance between the allowed space of the modes and the number of constraints we impose:

$$n_{\text{dof}} + n - 1 = n_{\text{con}}. \quad (26)$$

This is a generalization of the Maxwell condition, $n_{\text{dof}} = n_{\text{con}}$, that permits topological modes a system's surface. Consider in particular the case $n = 2$, with one additional constraint per unit cell above the Maxwell point. In this case, we would expect zero modes to appear only at particular values of z_1, z_2 which will, in general, not have unit magnitude. Thus, such modes will grow as one moves toward a particular corner, and are *corner modes*. In a new scheme of higher-order topological polarization, n th-order modes are those that occur on surface elements n dimensions smaller than the bulk. Conventional edge modes are first-order, appearing on the 0D end of a 1D chain, the 1D edge of a 2D system, or the 2D surface of a 3D system. Second-order modes appear at the corners of 2D systems and the 1D hinges of 3D systems. Since $n \leq D_c$, third-order polarization can appear only in the corners of 3D systems.

Considering the possibility of such modes, we must consider whether the bulk-boundary correspondence of Eq. (23) extends to such non-Maxwell systems. As demonstrated in Saremi and Rocklin (2018), this principle does extend conceptually, but the lack of a square matrix, which can be reduced essentially to a scalar by taking its determinant, complicates the mathematics considerably. As before, one can consider the space of all possible modes corresponding to a particular corner, for example those with $|z_1| < 1, |z_2| < 1$ and in particular the boundary of this space, where either $|z_1| = 1, |z_2| < 1$ or $|z_2| < 1, |z_2| = 1$. That is, the

boundary of the space of corner modes is the space of modes on the adjacent edges. One can map from modes in this space to the space of constraints, which is guaranteed via Eq. (26) to be of the same dimension. In this case, with complex-analytic expressions, the number of times this map covers the space [the generalization of the winding number of the winding number of Eq. (23)] is the number of corner modes.

This notion of higher-order topological invariants associated with rigidity matrices has been enumerated by Roychowdhury and Lawler, who classify topological invariants based on three symmetry classes, the dimension of the homotopy group and the amount by which the number of constraints differs from the degrees of freedom (Roychowdhury and Lawler 2018). In addition to the integer topological invariants discussed above, these include things such as Z_2 (binary) invariants. Additional topologically protected modes consistent with this scheme were recently identified at the interface between systems of over-constrained periodic chains with a certain symmetry (Kedia et al. 2021).

Alternate Formulations

The condition for linear zero modes Eq. (4) suffices to describe both finite-energy and rigid deformations. However, it is not the only way of characterizing a rigid deformation. Consider, in particular, the rigid deformations of a two-dimensional planar graph such as the kagome lattice. Such deformations translate and rotate bonds without stretching them. Consequently, we may characterize such a mode by the infinitesimal angle it rotates each bond. Such rotations automatically ensure bonds do not stretch, but they introduce an additional closure requirement, that any closed loop around bonds remains closed. This is a discrete version of *mechanical compatibility*, the requirement that a deformation or strain tensor correspond to a valid spatial embedding. The condition here is

$$\sum_i \mathbf{r}_i \theta_i = 0, \quad (27)$$

where the sum is over all edges in a closed loop. Here, $\mathbf{r}_i$ denotes the vector pointing from one end

to the other of a bond and θ_i the infinitesimal rotation of the bond. For a planar graph, if this condition is met on every irreducible loop around an open pore, it is also met on every loop composed therefrom. More properly, this sum should involve vectors perpendicular to the original bond vectors, but a common 90 degree rotation can be applied to place the expression in terms of the original vectors. Notably, Eq. (27) bears a close resemblance to the condition on a state of self stress, Eq. (9).

Such formulations are not necessarily superior to the conventional language of displacements, but they do offer certain advantages. Consider, for example, the deformed kagome lattice, which would normally require a 6×6 rigidity matrix to represent the displacements in two dimensions of the three particles and the constraints of the six bonds. In contrast, this formulation needs only describe the two orientational degrees of freedom of the two triangular pieces and the two-dimensional closure condition around the hexagonal pore, with the four additional degrees of freedom becoming trivial because the two triangular pieces are rigid. This formulation can be used to demonstrate that the deformed kagome cannot possess Weyl points, unlike another Maxwell lattice, the deformed square. Moreover, this notion of an alternate formulation for rigid deformations has greater bearing on the origami that we next consider.

Origami

A case of particular interest is triangulated origami, which consists of rigid triangular faces allowed to rotate freely along creases. A rigid embedding can then be described via a set of vertex positions that do not stretch any faces. However, a triangular face remains unstretched if and only if its edges remain unstretched (in contrast, a quadrilateral face could bend along a diagonal without stretching any of its edges). Thus, the rigid modes of origami correspond precisely to those of a system of particles at each of its vertices and bonds along each of its edges. Naively, one would then expect that topological polarization may occur. Indeed, triangulated periodic origami is particularly well-suited

to this as it is automatically mechanically critical. This can be seen via Euler's formula for the polyhedron, in which the numbers of vertices, faces, and edges are related via

$$V + F - E = \chi. \quad (28)$$

In the periodic triangulated case, each face has three edges but each edge appears along two faces, so to avoid double-counting we have $E = (3/2)F$. Since the Euler characteristic χ vanishes on a torus, including the flat torus to which periodic boundary conditions correspond, this implies that

$$E = 3V \quad (29)$$

for any triangulated surface. Thus, since each vertex can displace in three dimensions, we see that mechanical criticality is assured.

However, when such surfaces were generated, it was found exhaustively that their topological polarization vanished (Chen et al. 2016). This can be explained by considering a feature that makes such triangulations special and non-generic among all such frames. For such a surface, one may describe the change in shape of the system as a series of changes to the angles along edges between adjacent faces (the dihedral angles). One may not choose these arbitrarily, but only so that the total change in orientation around each vertex vanishes. In general, this change in orientation would be described via an element of $SO(3)$, as described by belcastro and Hull (Hull et al. 2002). For infinitesimal linear changes, however, the condition simplifies to

$$0 = \sum_{\alpha} \phi_{\alpha} \hat{r}_{\alpha}, \quad (30)$$

where the α index labels edges emanating from a single vertex along directions $\hat{r}_{\alpha}$ and ϕ_{α} describes the change in the dihedral angle along each edge. This condition, which must be satisfied at every vertex, has the precise form of a state of self stress in Eq. (9). Consequently, the (normalized) tensions in a state of self stress are exactly the angle changes of a zero mode (McInerney et al. 2020).

Unlike in the general case, in origami the states of self stress and zero modes really do map onto one another. Note that previously we had mechanical criticality because $E = 3V$ and each edge had one constraint and each vertex had three degrees of freedom. Now we still have criticality in this picture because each edge has one degree of freedom and each vertex has three constraints.

This duality between zero modes and states of self stress has important consequences for the topological character of origami zero modes. In general, in a Maxwell lattice a zero mode at a given complex wavevector implies a state of self stress at the *opposite* wavevector and vice versa, via Eq. (21). Now, however, this vertex duality means that a state of self stress at a wavevector implies a zero mode at the *same* wavevector. Thus, where for a general frame it was possible to have, for example, two zero modes on the left edge and two states of self stress on the right, in origami it is only possible to have equal numbers of zero modes on the left and right edges.

This feature has additional impact on the origami system. In particular, Weyl points emerged generically as zero-dimensional points in 2D Brillouin Zones of Maxwell lattices. This is because these correspond to places in which the determinant of the rigidity matrix vanishes. The real part of this matrix should vanish on a 1D subset of the 2D Brillouin Zone and the imaginary part should vanish on another 1D subset, such that the intersections are generically 0D Weyl points. In the origami case, however, the fact that a zero mode existing at some complex z comes paired with another at $1/z$ implies that the determinant function $d(z)$ is proportional to a "palindromic" polynomial in z such that the real coefficients of opposite powers of z are equal. This means that, up to a trivial gauge-dependent phase factor, the determinant function is real. This means that the requirement that its imaginary part vanishes becomes trivial and generically zero modes appear on 1D lines in the 2D Brillouin Zone. Further, there is a new Z_2 topological invariant, the sign of the determinant of the rigidity matrix, which flips value on either side of this line of zero modes. This behavior, which falls within the classification scheme of (Roychowdhury and Lawler

2018), has been predicted in both real origami (McInerney et al. 2020) and in the low-energy excitations of 2D frustrated magnetic systems that can be mapped onto origami (Roychowdhury et al. 2018).

Continuum Systems

Rigidity theory is naturally granular, or atomic, in the sense of having discrete vertices and edges. However, despite the atomic nature of elemental and molecular matter, over longer length scales this gives rise to continuum behavior as systems undergo deformations described not by sets of displacements but by displacement fields $\mathbf{u}(\mathbf{r})$. Linear elasticity is a well-developed theory which maps strain tensors, symmetrized gradients of displacements, onto stress tensors, whose divergences yield body forces. In this, then, conventional elasticity resembles a map between displacements and forces, a dynamical matrix, which due to mechanical reciprocity cannot display topological polarization. This raises the question of how such polarization can manifest itself in the continuum limit, in which the Brillouin zone and hence the notion of a compact region of state space seems to recede.

This challenge was addressed in two works in 2020 (Saremi and Rocklin 2020; Sun and Mao 2020). Here, the approach taken by Saremi and Rocklin is sketched. There, one begins with the linear rigidity map between extensions and displacements in a periodic cell Eq. (19). Treating the cell index as a continuous position vector allows one to express the extensions at a point in terms of continuous displacement fields. Due to intercellular bonds, these extensions are affected by gradients of the fields. In this way, one obtains a differential operator between the displacements of the microscopic degrees of freedom and the microscopic constraints.

In order to make connection with elasticity, one considers smooth displacement fields applied equally to each microscopic particle. This generally leads to extensions of bonds and unbalanced forces acting on each particle. However, following microscopic rearrangements in order to

alleviate these forces, the only extensions that remain are those that lie in the space of states of self stress. In a Maxwell system, the number of such self stresses is equal to the dimension of the embedding space. Consequently, the resulting reduced, continuum rigidity map is square, so that microscopic criticality maps onto macroscopic criticality.

This map shares a number of features with its discrete analog. Most notably, there is a corresponding equilibrium map that maps from continuous states of self stress onto force fields. These two maps are in a certain sense transposes of one another evaluated at opposite wavevectors, just as in the microscopic case.

However, while the principle of topological polarization does indeed carry over to the continuum, it is also transformed. Modes on the left and right edges can no longer be expressed as the interior and exterior of the unit circle in the 2D plane. Now, these modes are most easily expressed as the upper and lower half-planes, neither of which is compact, limiting the application of the argument principle. However, by taking the continuum limit carefully, one can demonstrate that a similar topological invariant emerges that yields not the number of modes on the left or right edges but rather the difference between the two. That is,

$$N_L - N_R = \frac{1}{\pi} \int dq_i \partial_{q_i} \arg \det(\mathbf{C}), \quad (31)$$

where the regularization scheme required to perform the integral in the continuum is described in Saremi and Rocklin (2020). This result, based in the continuum rather than in periodic microstructures, closely resembles, yet conceptually modifies that of Kane and Lubensky (2014). This raises the question of how generally the principle that asymmetrical structures may serve to direct flexibility may be extended.

Conclusion

In recent years, tight connections have been drawn between the static modes (zero modes and

states of self stress) of mechanical frames and topological states. This connection has been used to create, direct, and protect novel modes. A fundamental advance came in Kane and Lubensky's 2014 result for periodic Maxwell (critically coordinated) lattices. Many subsequent results have come for systems with additional geometric complexity, including topological defects (Paulose et al. 2015), nonlinearities (Chen et al. 2014), imbalances between constraints and degrees of freedom (Saremi and Rocklin 2018; Roychowdhury and Lawler 2018; Kedia et al. 2021), continuous degrees of freedom (Saremi and Rocklin 2020; Sun and Mao 2020; Bartolo and Carpentier 2019), and surfaces and non-mechanical constraints (Roychowdhury et al. 2018; Murugan and Vaikuntanathan 2017). Developments have also come from protected bulk modes (Rocklin et al. 2016; Stenull et al. 2016) and mechanical response (Rocklin 2017).

Future advances may come by exploring additional geometries of mechanical systems. Dynamical topologically protected modes have already been demonstrated in amorphous systems (Mitchell et al. 2018) via real-space techniques – might the static modes of such structures also display topological classes?

Despite the extensive work on topological mechanics of dynamical modes (Süsstrunk and Huber 2016), the connection to static modes remains to be developed. Dynamic topological mechanics is further enriched by the possibility of thermal (Rocklin et al. 2018) and quantum fluctuations (Mizoguchi et al. 2021) and perhaps by the incorporation of active matter (Shankar et al. 2020).

In summary, recent years have revealed that beyond the topological dynamical modes lie topological zero modes and state of self stress that determine a system's low-frequency mechanical response. New topological invariants lead to novel and robust forms of flexibility, centered around proximity to a mechanical critical point.

This behavior has been demonstrated in increasingly complex structures, with the promise of further discoveries lying in systems with aperiodicity, nonlinearity, fluctuations, and other complex, challenging features that lie beyond the Brillouin Zone.

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Glasses and Aging, A Statistical Mechanics Perspective on

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Article Outline

Glossary
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Phenomenology
Taxonomy of “Glasses” in Science
Numerical Simulations
Dynamic Heterogeneity
Theory of the Glass Transition
Mean-Field Theory of the Amorphous Phase
New Computational Methods
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Glossary

We start with a few concise definitions of the most important concepts discussed in this entry.

Glass transition For molecular liquids, the glass transition denotes a crossover from a viscous

liquid to an amorphous solid. Experimentally, the crossover takes place at the glass temperature, T_g , conventionally defined as the temperature where the liquid's viscosity reaches the arbitrary value of 10^{12} Pa.s. The glass transition more generally applies to many different condensed matter systems where a crossover or, less frequently, a true phase transition takes place between an ergodic phase and a frozen, amorphous glassy phase.

Aging In the glass phase, disordered materials are characterized by relaxation times that exceed common observation timescales, so that a material quenched in its glass phase never reaches equilibrium (neither a metastable equilibrium). It exhibits instead an aging behavior during which its physical properties keep evolving with time.

Dynamic heterogeneity Relaxation spectra of dynamical observables, for example, the dynamical structure factor, are very broad in supercooled liquids. This is associated to a spatial distribution of timescales: at any given time, different regions in the liquid relax at different rates. Since the supercooled liquid is ergodic, slow regions eventually become fast, and vice versa. Dynamic heterogeneity refers to the existence of these nontrivial spatiotemporal fluctuations in the local dynamical behavior, a phenomenon observed in virtually all disordered systems with slow dynamics.

Effective temperature An aging material relaxes very slowly, trying (in vain) to reach its equilibrium state. During this process, the system probes states that do not correspond to thermodynamic equilibrium, so that its thermodynamic properties cannot be rigorously defined. Any practical measurement of its temperature becomes a frequency-dependent operation. A “slow” thermometer tuned to the relaxation timescale of the aging system measures an effective temperature corresponding to the ratio between spontaneous fluctuations (correlation) and linear response (susceptibility). This

corresponds to a generalized form of the fluctuation-dissipation theorem for off-equilibrium materials.

Frustration Impossibility of simultaneously minimizing all the interaction terms in the energy function of the system. Frustration might arise from quenched disorder (as in the spin glass models), from competing interactions (as in geometrically frustrated magnets), or from competition between a “locally preferred order,” and global, for example, geometric, constraints (as in hard spheres packing problems).

Marginal Stability Systems are marginally stable when the number of external inputs controlling their stability is just enough to constrain all their degrees of freedom (think of a table with three legs). Marginally stable systems display an excess of zero-energy modes which makes them highly susceptible to external perturbations, and prone to extensive rearrangements.

Definition of the Subject

Glasses belong to a seemingly well-known state of matter: we easily design glasses with desired mechanical or optical properties on an industrial scale, and they are widely present in our daily life. Yet, a deep microscopic understanding of the glassy state of matter remains a challenge for condensed matter physicists (Angell 1995; Debenedetti and Stillinger 2001; Berthier and Biroli 2011). Glasses share similarities with crystalline solids (they are both mechanically rigid), but also with liquids (they both have similar disordered structures at the molecular level). It is mainly this mixed character that makes them fascinating objects, even to nonscientists.

A glass can be obtained by cooling the temperature of a liquid below its glass temperature, T_g . The quench must be fast enough, such that the more standard first-order phase transition toward the crystalline phase is avoided. The glass “transition” is not a thermodynamic transition at all, since T_g is only empirically defined as the temperature below which the material has become too

viscous to flow on a “reasonable” timescale (and it is hard to define the word “reasonable” in any reasonable manner). Therefore, T_g cannot play a very fundamental role, as a phase transition temperature would. It is simply the temperature below which the material looks solid on the timescale of the observer. When quenched in the glass phase below T_g , liquids slowly evolve toward an equilibrium state they will never reach on experimental timescales. Physical properties are then found to evolve slowly with time in far from equilibrium states, a process known as “aging” (Struik 1977).

Describing theoretically and quantifying experimentally the physical mechanisms responsible for the viscosity increase of liquids approaching the glass transition and for aging phenomena below the glass transition certainly stand as central open challenges in condensed matter physics. Since statistical mechanics aims at understanding the collective behavior of large assemblies of interacting objects, it comes as no surprise that it is a central tool in the glass field. We shall therefore summarize the understanding gained from statistical mechanics perspectives into the problem of glasses and aging.

The subject has quite broad implications. A material is said to be “glassy” when its typical relaxation timescale becomes of the order of, and often much larger than, the typical duration of an experiment or a numerical simulation. Under this generic definition, a large number of systems can be considered as glassy (Young 1998). One can be interested in the physics of liquids (window glasses are then the archetype), in “hard” condensed matter (for instance type II superconductors in the presence of disorder such as high- T_c superconductors), charge density waves or spin glasses, “soft” condensed matter with numerous complex fluids such as colloidal assemblies, emulsions, foams, but also granular materials, proteins, etc. All these materials exhibit, in a part of their phase diagrams, some sort of glassy dynamics characterized by a very rich phenomenology with effects such as aging, hysteresis, creep, memory, effective temperatures, rejuvenation, dynamic heterogeneity, and nonlinear response.

This long list explains why this research field has received increasing attention from physicists

in the last four decades. “Glassy” topics now go much beyond the physics of simple liquids (glass transition physics), and models and concepts developed for one system often find applications elsewhere in physics, from algorithmics to biophysics (Bouchaud et al. 2011). Motivations to study glassy materials are numerous. Glassy materials are everywhere around us and therefore obviously attract interest beyond academic research. At the same time, the glass conundrum provides theoretical physicists with deep fundamental questions since classical tools are sometimes not sufficient to properly account for the glass state. Moreover, numerically simulating the dynamics of microscopically realistic material on timescales that are experimentally relevant remains a difficult challenge, even with modern computers.

Studies on glassy materials constitute an exciting research area where experiments, simulations, and theoretical calculations can meet, and where both applied and fundamental problems are considered. How can one observe, understand, and theoretically describe the rich phenomenology of glassy materials? What are the fundamental quantities and concepts that emerge from these descriptions?

The outline of the entry is as follows. In section “[Phenomenology](#)” the phenomenology of glass-forming liquids is discussed. In section “[Taxonomy of “Glasses” in Science](#)” different types of glasses are described. We then describe how computer simulations can provide deep insights into the glass problem in section “[Numerical Simulations](#).” The issue of dynamic heterogeneity is tackled in section “[Dynamic Heterogeneity](#).” The main theoretical perspectives currently available in the field are then summarized in section “[Theory of the Glass Transition](#).” The mean-field analysis of the amorphous solid phase is reviewed in section “[Mean-Field Theory of the Amorphous Phase](#).” In section “[New Computational Methods](#),” we discuss novel developments in computational studies. Aging and off-equilibrium phenomena occupy section “[Aging and Off-Equilibrium Dynamics](#).” Finally, issues that seem important for future research are discussed in section “[Future Directions](#).”

Phenomenology

Basic Facts

A vast majority of liquids (molecular liquids, polymeric liquids, etc.) form a glass if cooled fast enough in order to avoid the crystallization transition (Angell 1995). Typical values of cooling rate in laboratory experiments are 0.1–100 K/min. The metastable phase reached in this way is called “supercooled liquid.” In this regime the typical timescales increase in a dramatic way and they end up to be many orders of magnitudes larger than microscopic timescales at T_g , the glass transition temperature.

For example, around the melting temperature T_m , the typical timescale T_α on which density fluctuations relax is of the order of $\sqrt{ma^2/K_B T}$, which corresponds to few picoseconds (m is the molecular mass, T the temperature, K_b the Boltzmann constant, and a is a typical distance between molecules). At T_g , which as a rule of thumb is about $\frac{2}{3}T_m$, this timescale τ_α has become of the order of 100 s, that is, 14 orders of magnitude larger! This phenomenon is accompanied by a concomitant increase of the shear viscosity η . This can be understood by a simple Maxwell model in which η and τ are related by $\eta = G_\infty \tau_\omega$ where G_∞ is the instantaneous (elastic) shear modulus which does not vary considerably in the supercooled regime. In fact, viscosities at the glass transition temperature are of the order of 10^{12} Pa.s. In order to grasp how viscous this is, recall that the typical viscosity of water (or wine) at ambient temperature is of the order of 10^{-2} Pa.s. How long would one have to wait to drink a glass of wine with a viscosity 10^{14} times larger?

As a matter of fact, the temperature at which the liquid does not flow anymore and becomes an amorphous solid, called a “glass,” is protocol dependent. It depends on the cooling rate and on the patience of the person carrying out the experiment: solidity is a timescale-dependent notion. Pragmatically, T_g is defined as the temperature at which the shear viscosity is equal to 10^{13} Poise (also 10^{12} Pa.s).

The increase of the relaxation timescale of supercooled liquids is remarkable not only because of the large number of decades involved

but also because of its temperature dependence. This is vividly demonstrated by plotting the logarithm of the viscosity (or of the relaxation time) as a function of T_g/T , as in Fig. 1. This is called the “Angell” plot (Angell 1995), which is very helpful in classifying supercooled liquids. A liquid is called strong or fragile depending on its position in the Angell plot. Straight lines correspond to “strong” glass-formers and to an Arrhenius behavior. In this case, one can extract from the plot an effective activation energy, suggesting quite a simple mechanism for relaxation, for instance by “breaking” locally a chemical bond. The typical relaxation time is then dominated by the energy barrier to activate this process and, hence, has an Arrhenius behavior. Window glasses fall in this category. (The terminology “strong” and “fragile” is not related to the mechanical properties of the glass but to the evolution of the short-range order close to T_g . Strong liquids, such as SiO_2 , have a locally tetrahedric structure which persists both below and above the

glass transition contrary to fragile liquids whose short-range amorphous structure disappears rapidly upon heating above T_g .) If one tries to define an effective activation energy for fragile glass-formers using the slope of the curve in Fig. 1, then one finds that this energy scale increases when the temperature decreases, a “super-Arrhenius” behavior. This increase of energy barriers immediately suggests that glass formation is a collective phenomenon for fragile supercooled liquids. Support for this interpretation is provided by the fact that a good fit of the relaxation time or the viscosity is given by the Vogel-Fulcher-Tamman law (VFT):

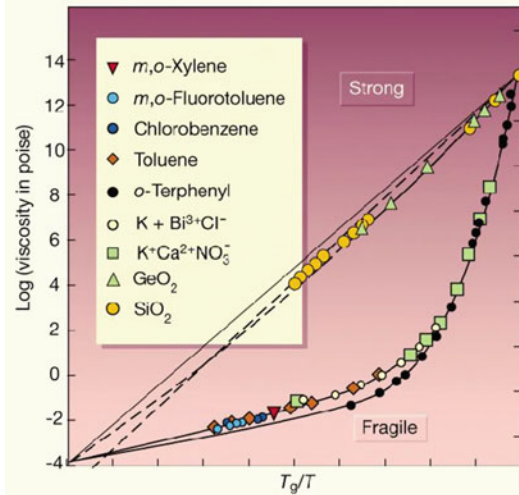
$$\tau_\alpha = \tau_0 \exp \left[\frac{DT_0}{(T - T_0)} \right], \quad (1)$$

which suggests a divergence of the relaxation time, and therefore a phase transition of some kind, at a finite temperature T_0 . A smaller D in the VFT law corresponds to a more fragile glass. Note that there are other comparably good fits of these curves, such as the Bässler law (Bässler 1987),

$$\tau_\alpha = \tau_0 \exp \left(K \left(\frac{T^*}{T} \right)^2 \right), \quad (2)$$

that only lead to a divergence at zero temperature. Actually, although the relaxation time increases by 14 orders of magnitude, the increase of its logarithm, and therefore of the effective activation energy is very modest, and experimental data do not allow one to unambiguously determine the true underlying functional law without any reasonable doubt. For this and other reasons, physical interpretations in terms of a finite temperature phase transition must always be taken with a grain of salt.

However, there are other experimental facts that shed some light and reinforce this interpretation. Among them is an empirical connection found between kinetic and thermodynamic behaviors. Consider the part of the entropy of liquids, S_{exc} , which is in excess compared to the entropy of the corresponding crystal. Once this quantity, normalized by its value at the melting temperature, is



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 1 Arrhenius plot of the viscosity of several glass-forming liquids approaching the glass temperature T_g (Debenedetti and Stillinger 2001). For “strong” glasses, the viscosity increases in an Arrhenius manner as temperature is decreased, $\log \eta \sim E/(K_s T)$, where E is an activation energy and the plot is a straight line, as for silica. For “fragile” liquids, the plot is bent and the effective activation energy increases when T is decreased toward T_g , as for ortho-terphenyl

plotted as a function of T , a remarkable connection with the dynamics emerges. As for the relaxation time one cannot follow this curve below T_g in thermal equilibrium. However, extrapolating the curve below T_g apparently indicates that the excess entropy vanishes at some finite temperature, called T_K , which is very close to zero for strong glasses and, generically, very close to T_0 , the temperature at which a VFT fit diverges. This coincidence is quite remarkable: for materials with glass transition temperatures that vary from 50 K to 1000 K the ratio T_K/T_0 remains close to 1, up to a few percent. Examples reported in Richert and Angell (1998) are provided in Table 1.

The chosen subscript for T_K stands for Kauzmann (1948), who recognized T_K as an important temperature scale for glasses. Kauzmann further claimed that some change of behavior (phase transition, crystal nucleation, etc.) must take place above T_K , because below T_K the entropy of the liquid, a disordered state of matter, becomes less than the entropy of the crystal, an ordered state of matter. The situation that seemed paradoxical at that time is actually not a serious conceptual problem (Berthier and Biroli 2011; Berthier et al. 2019a). There is no general principle that constrains the entropy of the liquid to be larger than that of the crystal. As a matter of fact, the crystallization transition for hard spheres takes place precisely because the crystal becomes the state with the largest entropy at sufficiently high density (Holyst 2001).

On the other hand, the importance of T_K stands, partially because it is experimentally very close to T_0 . Additionally, the quantity S_{exc} which vanishes at T_K is thought to be a proxy for the so-called configurational entropy, S_c , which quantifies the number of metastable states. A popular physical picture due to Goldstein (1969) is that close to T_g

the system explores a part of the energy landscape (or configuration space) which is full of minima separated by barriers that increase when temperature decreases. The dynamic evolution in the energy landscape would then consist in a rather short equilibration inside a minimum followed by infrequent “jumps” between different minima. At T_g the barriers between states become so large that the system remains trapped in one minimum, identified as one of the possible microscopic amorphous configurations of a glass. Following this interpretation, one can split the entropy into two parts. A first contribution is due to the fast relaxation inside one minimum and a second one, called the “configurational” entropy, counts the number of metastable states: $S_c = \log N_{\text{metastable}}$. Assuming that the contribution to the entropy due to the “vibrations” around an amorphous glass configuration is not very different from the entropy of the crystal, one finds that $S_{\text{exc}} \approx S_c$. In that case, T_K would correspond to a temperature at which the configurational entropy vanishes. This in turn would lead to a discontinuity (a downward jump) of the specific heat and would truly correspond to a thermodynamic phase transition.

Static and Dynamic Correlation Functions

At this point the reader might have reached the conclusion that the glass transition may not be such a difficult problem: there are experimental indications of a diverging timescale and a concomitant singularity in the thermodynamics. It simply remains to find static correlation functions displaying a diverging correlation length related to the emergence of “amorphous order,” which would indeed classify the glass transition as a standard second-order phase transition. Remarkably, this conclusion remains an open and debated question despite several decades of research.

Glasses and Aging, A Statistical Mechanics Perspective on,
Table 1 Values of glass transition temperature, VFT singularity and Kauzmann temperatures for four supercooled liquids (Richert and Angell 1998)

Substance	<i>o</i> -terphenyl	2-methyltetrahydrofuran	<i>n</i> -propanol	3-bromopentane
T_g	246	91	97	108
T_0	202.4	69.6	70.2	82.9
T_K	204.2	69.3	72.2	82.5
T_K/T_0	1.009	0.996	1.028	0.995

Simple static correlation functions are quite featureless in the supercooled regime, notwithstanding the dramatic changes in the dynamics. A simple static quantity is the structure factor defined by

$$S(q) = \left\langle \frac{1}{N} \delta \rho_{\mathbf{q}} \delta \rho_{-\mathbf{q}} \right\rangle, \quad (3)$$

where the Fourier component of the density reads

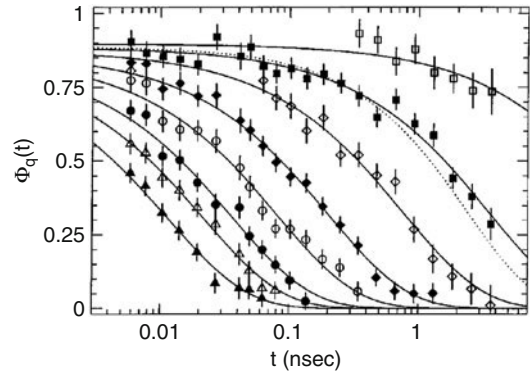
$$\delta \rho_{\mathbf{q}} = \sum_{i=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_i} - \frac{N}{V} \delta_{\mathbf{q},0}, \quad (4)$$

with N the number of particles, V the volume, and $\mathbf{r}_i$ the position of particle i . The structure factor measures the spatial correlations of particle positions, but it does not show any diverging peak in contrast to what happens, for example, at the liquid-gas critical point where there is a divergence at small $\mathbf{q}$. More complicated static correlation functions have been studied (Debenedetti 1996), especially in numerical work, but until now there are no strong indications of a diverging, or at least substantially growing, static lengthscale (Menon and Nagel 1995; Fernández et al. 2006; Cavagna et al. 2007). A snapshot of a supercooled liquid configuration in fact just looks like a glass configuration, despite their widely different dynamic properties (Berthier et al. 2019a). What happens then at the glass transition? Is it a transition or simply a dynamic crossover? A more refined understanding can be gained by studying dynamic correlations or response functions.

A dynamic observable studied in light and neutron scattering experiments is the intermediate scattering function,

$$F(\mathbf{q}, t) = \left\langle \frac{1}{N} \delta \rho_{\mathbf{q}}(t) \delta \rho_{-\mathbf{q}}(0) \right\rangle. \quad (5)$$

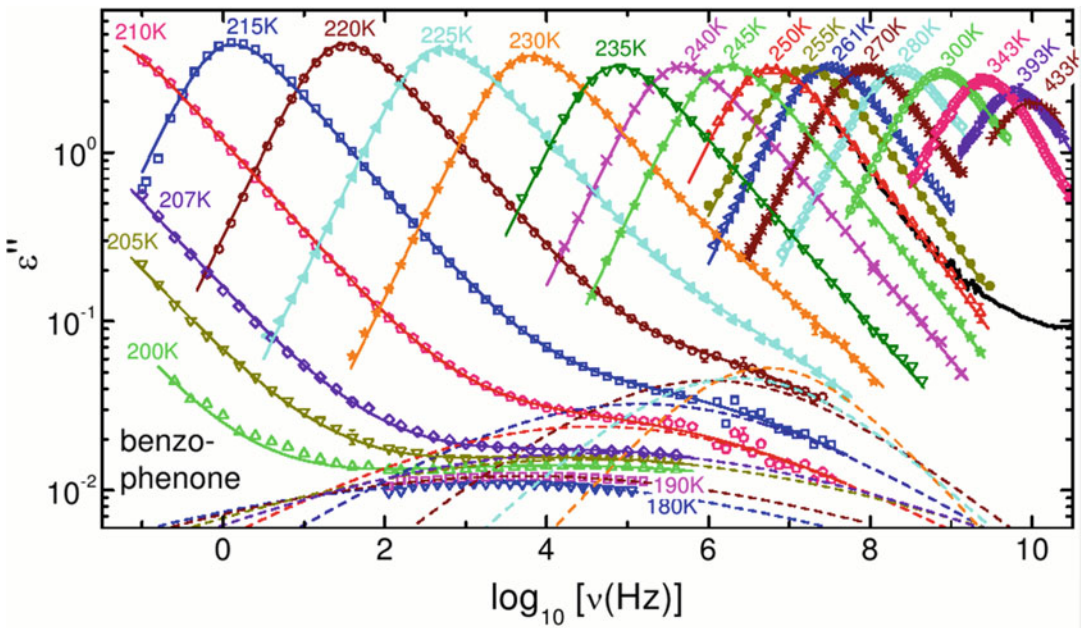
Different $F(\mathbf{q}, t)$ measured by neutron scattering in supercooled glycerol (Wuttke et al. 1996) are shown for different temperatures in Fig. 2. These curves show a first, rather fast, relaxation to a plateau followed by a second, much slower, relaxation. The plateau is due to the fraction of density fluctuations that are frozen on



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 2 Temperature evolution of the intermediate scattering function normalized by its value at time equal to zero for supercooled glycerol (Wuttke et al. 1996). Temperatures decrease from 413 K to 270 K from right to left. The solid lines are fit with a stretched exponential with exponent $\beta = 0.7$. The dotted line represents another fit with $\beta = 0.82$

intermediate timescales, but eventually relax during the second relaxation. The latter is called “alpha-relaxation,” and corresponds to the structural relaxation of the liquid. This plateau is akin to the Edwards-Anderson order parameter q_{EA} defined for spin glasses, which measures the fraction of frozen spin fluctuations (Binder and Kob 2011). Note that q_{EA} continuously increases from zero at the spin glass transition. Instead, for structural glasses, a finite plateau value already appears above any transition.

The intermediate scattering function can be probed only on a relatively small regime of temperatures. In order to track the dynamic slowing down from microscopic to macroscopic timescales, other correlators have been studied. A popular one is obtained from the dielectric susceptibility, which is related by the fluctuation-dissipation theorem to the time correlation of polarization fluctuations. It is generally admitted that different dynamic probes reveal similar temperature dependencies of the relaxation time. The temperature evolution of the imaginary part of the dielectric susceptibility, $\epsilon''(\omega)$, is shown in Fig. 3, which covers a very wide temperature window (Pardo et al. 2007). At high temperature, a good representation of the data is given by a Debye law, $\epsilon(\omega) = \epsilon(\infty) + \Delta\epsilon/(1 + i\omega\tau_a)$, which corresponds to an exponential



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 3 Temperature evolution of the dielectric susceptibility of the glass-former benzophenone measured over more than 10 decades of relaxation times (Pardo et al.

2007). Dynamics slows down dramatically as temperature is decreased and relaxation spectra become very broad at low temperature

relaxation in the time domain. When temperature is decreased, however, the relaxation spectra become very broad and strongly non-Debye. One particularly well-known feature of the spectra is that they are well fitted, in the time domain, for times corresponding to the alpha relaxation with a stretched exponential, $\exp(-(t/\tau_\alpha)^\beta)$. In the Fourier domain, forms such as the Havriliak-Negami law are used, $\epsilon(\omega) = \epsilon(\infty) + \Delta\epsilon/(1 + (i\omega\tau_\alpha)^\alpha)^\gamma$, which generalize the Debye law. The exponents β , α , and γ depend in general on temperature and on the particular dynamic probe chosen, but they capture the fact that relaxation is increasingly non-exponential when T decreases toward T_g . A connection was empirically established between fragility and degree of non-exponentiality, more fragile liquids being characterized by broader relaxation spectra (Debenedetti and Stillinger 2001).

To sum up, there are many remarkable phenomena that take place when a supercooled liquid approaches the glass transition. Striking ones have been presented, but many others have been left out for lack of space (Angell 1995; Debenedetti and Stillinger 2001; Debenedetti 1996; Binder and

Kob 2011; Berthier and Ediger 2016). We have discussed physical behaviors, relationships, or empirical correlations observed in a broad class of materials. This is quite remarkable and suggests that there is some physics (and not only chemistry) to the problem of the glass transition, which we see as a collective (critical?) phenomenon which should be relatively independent of microscopic details. This justifies our statistical mechanics perspective on this problem.

Taxonomy of “Glasses” in Science

We now introduce a wider range of systems whose phenomenological behavior is close or related to the one of glass-forming liquids, showing that glassiness is truly ubiquitous. It does not only appear in many different physical situations but also in more abstract contexts, such as computer science.

Colloidal Glass Transition

Colloidal suspensions consist of large particles suspended in a solvent (Larson 1999). The typical

radii of the particles are in the range of $R = 1\text{--}500$ nm. The solvent, which is at equilibrium at temperature T , renders the short-time dynamics of the particles Brownian. The microscopic timescale for this diffusion is given by $\tau = R^2/D$, where D is the short-time self-diffusion coefficient. A typical value is of the order of $\tau \sim 1$ ms, which is thus much larger than microscopic timescales for molecular liquids (in the picosecond regime). The interaction potential between particles depends on the systems, and this large tunability makes colloids very attractive objects for technical applications. A particularly relevant case, on which we will focus in the following, is a purely hard sphere potential, which is zero when particles do not overlap and infinite otherwise. In this case the temperature scale becomes an irrelevant number, apart from a trivial rescaling of the microscopic timescale. Colloidal hard sphere systems have been intensively studied (Larson 1999) in experiments, simulations, and theory, varying their density ρ , or their volume fraction $\varphi = \frac{4}{3}\pi R^3 \rho$. Hard spheres display a fluid phase from $\varphi = 0$ to intermediate volume fractions, a freezing-crystallization transition at $\varphi \simeq 0.494$, and a melting transition at $\varphi \simeq 0.545$. Above this latter value the system can be compressed until the close packing point $\varphi \simeq 0.74$, which corresponds to the FCC crystal. Interestingly for our purposes, a small amount of size polydispersity can suppress crystallization. In this case, the system can be “supercompressed” above the freezing transition without nucleating the crystal, at least on experimental timescales. In this regime the relaxation timescale increases very fast (Pusey and VanMegen 1986). At a packing fraction $\varphi_g \simeq 0.58 - 0.60$ it becomes so large compared to typical experimental timescales that the system does not relax anymore: it is frozen. This “colloidal glass transition” is obviously reminiscent of the glass transition of molecular systems. In particular, the location φ_g of the colloidal glass transition is as ill-defined as the glass temperature T_g .

Actually, the phenomena that take place when increasing the volume fraction are analogous to the ones seen in molecular supercooled liquid when decreasing temperature: the relaxation

timescales increases very fast and can be fitted (Cheng et al. 2002; Berthier and Witten 2009) by a VFT law in density similar to Eq. (1), dynamical correlation functions display a broad spectrum of timescales and develop a plateau, no static growing correlation length has been found, etc. Also the phenomenon of dynamic heterogeneity that will be addressed in section “[Dynamic Heterogeneity](#)” is also observed in colloids (Kegel and van Blaaderen 2000; Weeks et al. 2000). However, it is important to underline a major difference: because the microscopic timescale for colloids is so large, experiments can only track the first five decades of slowing down. A major consequence is that the comparison between the glass and colloidal transitions must be performed by focusing in both cases on the first five decades of the slowing down, which corresponds to relatively high temperatures in molecular liquids (Brambilla et al. 2009). Understanding how much and to what extent the glassiness of colloidal suspensions is related to the one of molecular liquids remains an active domain of research. Recently, by using colloids of smaller size and hence decreasing the microscopic timescale τ , it has been possible to explore a larger range of relaxation times (Hallett et al. 2018). This is a very promising research direction to explore the colloidal glassy regime.

Jamming Transition

Every day life offers many examples of jammed solids: grains and beans poured into a container, foams and emulsions produced by a large shear stress, sand and colloidal particles under very high pressure. Depending on how compressed they are, these materials behave as fluids or solids: a handful of sand will flow from our open hand, while we experience rigidity when closing the fist. Formally, the jamming transition is reached at infinite pressure when all the droplets, bubbles, or colloids are forced to come into enduring kissing contact with one another (Donev et al. 2004, 2005). All these systems share a fundamental feature: they can be considered athermal in the sense that thermal fluctuations at room temperature are, by far, not able to allow the system to explore its phase space.

As an immediate consequence, the glass and jamming transitions are of a very different nature. The former describes a fluid-to-solid transition in a system controlled by thermal fluctuations, and its location depends on the cooling or compression rate. The latter is a purely geometrical transition happening at $T = 0$ in the absence of any dynamics, but it also corresponds to the change between a viscous liquid to a solid mechanical response (Liu and Nagel 1998). In recent years, the connection between the two phenomena has been elucidated (Charbonneau et al. 2017), and both transitions can be observed under different physical conditions in the hard spheres model.

Granular Glass Transition

Driven granular media represent another family of systems that have recently been studied from the point of view of their glassiness. Grains are macroscopic objects and, as a consequence, are not affected by thermal fluctuations. A granular material is therefore frozen in a given configuration if no energy is injected into the system (Jaeger et al. 1996). However, it can be forced in a steady state by an external drive, such as shearing or tapping. The dynamics in this steady state shows remarkable similarities (and differences) with simple fluids. The physics of granular materials is a very wide subject (Jaeger et al. 1996). In the following we only address briefly what happens to a polydisperse granular fluid at very high packing fractions. As for colloids, the timescales for relaxation or diffusion increase very fast when density is increased, without any noticeable change in structural properties. It is now established (D'Anna and Grémaud 2001; Marty and Dauchot 2005; Keys et al. 2007) that many phenomenological properties of the glass and jamming transitions also occur in granular assemblies. Going beyond the mere analogy and understanding how much colloids and granular materials are related is a very active domain of research.

Active Glasses

Active matter has recently emerged as a new field in physics (Marchetti et al. 2013; Bechinger et al.

2016), fueled by the observation that systems such as a school fish, bacterial colonies, and biological tissues display physical properties and phase transitions which can be described by statistical physics tools, and captured by simplified theoretical models. Physical systems mimicking the behavior of natural systems have also been developed to perform controlled experiments on model systems of active materials. In particular, colloidal particles and macroscopic objects similar to the systems displaying a granular glass transition have also been developed so that these particles can become “active” (Deseigne et al. 2010; Theurkauff et al. 2012; Buttinoni et al. 2013), that is, self-motile objects that can move in the absence of thermal fluctuations, similar to animals, cells, or bacteria.

It is natural to expect that dense assemblies of active particles will undergo some form of dynamic arrest (Henkes et al. 2011; Angelini et al. 2011). As human beings, we are well aware that it becomes difficult to walk very fast in a dense crowd, as observed in the streets of large cities or in subway corridors at peak times. Indeed, there are several indications from experimental observations that a transition from a fluid-like state to an arrested glassy state can be observed in active materials (Angelini et al. 2011; Garcia et al. 2015; Mongera et al. 2018; Klongvessa et al. 2019).

From a conceptual viewpoint, the main difference between these observations and the glass transition observed in molecular and colloidal systems is that the driving force for single particle motion is not of thermal origin, but is instead chemical, mechanical, or biological. This means that any theoretical model for dense active materials must include some sort of nonequilibrium sources of microscopic motion and consequently the glassy phenomena that will be described must necessarily occur far from equilibrium (Berthier and Kurchan 2013). In that sense, the situation is conceptually not very different from the phenomenon of the granular glass transition discussed in the previous paragraph. The difference between the two essentially lies in the details of the driving motion, which very much resembles a quasi-

equilibrium thermal bath in granular glasses (Keys et al. 2007).

Several numerical and theoretical studies of the glass transition in active materials have been recently published, see Berthier et al. (2019b) for a specific review on this topic. In particular, the glassy dynamics of so-called self-propelled particles have received considerable attention (Ni et al. 2013; Berthier 2014; Mandal et al. 2016; Bi et al. 2016; Berthier et al. 2017a; Matoz-Fernandez et al. 2017). In these models, particles interacting with simple pair interactions (similar to the ones studied to model the equilibrium glass transition) are driven by active forces that tend to displace the particles in straight lines over a finite persistence length.

It is now understood that for dense active fluids, due to these nonequilibrium driving forces both the structure and the dynamics are very different from their equilibrium counterparts (Berthier et al. 2019b). It is observed that a large persistence length has a profound influence on the static correlations of the fluid since both density-density (as in Eq. (3)) and velocity-velocity correlation functions develop non trivial non-equilibrium features (Berthier et al. 2017a). As particle crowding is increased, slow dynamics develop and is accompanied by a phenomenology similar to that of equilibrium glassy materials, with motion becoming gradually arrested at large enough density or small enough activity. Dynamic arrest in dense active materials is therefore called a nonequilibrium glass transition (Berthier and Kurchan 2013). Understanding this new class of glassy dynamics is an exciting new direction for research.

Random Pinning Glass Transition

The standard control parameters used to induce a glass transition are temperature and pressure. A new way introduced in the 2000s is “random pinning” (Scheidler et al. 2002; Kim 2003), which consists in freezing the positions of a fraction c of particles from an equilibrium configuration of a supercooled liquid. Theoretical arguments (Cammarota and Biroli 2012) and numerical simulations (Berthier and Kob 2012; Karmakar and Procaccia 2011) suggested that the dynamics of

the remaining free particles slow down and undergo a glass transition by increasing c . The study of the random pinning glass transition has been the focus of several theoretical analyses (Cammarota and Biroli 2013; Krakoviack 2011, 2014; Szamel and Flenner 2013; Franz and Parisi 2013; Cammarota 2013; Franz et al. 2013; Phan and Schweizer 2018; Cammarota and Seoane 2016; Ikeda et al. 2017a) and numerical simulations (Berthier and Kob 2012; Kob and Berthier 2013; Charbonneau and Tarjus 2013; Karmakar and Parisi 2013; Chakrabarty et al. 2015, 2016; Kob and Coslovich 2014; Jack and Fullerton 2013; Fullerton and Jack 2014; Li et al. 2015; Angelani et al. 2018; Ozawa et al. 2018a; Niblett et al. 2018) in the decade 2005–2015. It has also been studied in experiments, in particular in colloidal glasses by optical microscopy (Gokhale et al. 2014, 2016; Ganapathi et al. 2018; Williams et al. 2018).

The interest in the “random-pinning glass transition” has been twofold. First, it represents a new way to test theories of the glass transition. In fact, RFOT theory and MCT (see section “Theory of the Glass Transition”) predict that it should have the same properties as the usual glass transition (Cammarota and Biroli 2012; Szamel and Flenner 2013), that is, increasing the pinned fraction c plays the same role as lowering the temperature. This phenomenon was studied and confirmed in Kob and Berthier (2013), where the equilibrium phase diagram of a randomly pinned glass-former was fully characterized. The dynamical behavior is not as well understood. Although it is clear that dynamics dramatically slows down when increasing c , hence the name “random-pinning glass transition,” it has proven difficult to disentangle trivial effects due to steric constraints from collective ones. In consequence, numerical simulations could not validate or disprove the competing predictions from dynamical facilitation theories (Jack and Berthier 2012) and RFOT theory (Cammarota and Biroli 2012). The other reason for the random pinning procedure was to produce configurations equilibrated very close to the glass transition (just after pinning, the remaining unpinning particles are in an equilibrium configuration for the constrained systems (Krakoviack 2010)). This

allowed to perform the first computational study of ultrastable glasses (Hocky et al. 2014), see below.

The random pinning procedure has interesting connections, similarities, and differences with other ways to constrain the dynamics of glassy liquids introduced in recent years. Those can be grouped in three main categories: modifications of the Hamiltonian (ϵ -coupling, see section “[Franz-Parisi Potential](#)”), in the dynamical rules (s -ensemble dynamics, see section “[s-Ensemble and Large Deviations](#)”), and in the space available to the system (liquids in quenched environments (Thalmann et al. 2000)).

Ultrastable Glasses

Glassy materials are typically prepared by slowly cooling or compressing a dense fluid across the glass transition described above. The glass transition temperature or density is set by the competition between an extrinsic time scale imposed by the experimentalist (for instance the duration of the experiment, or the cooling rate), and an intrinsic timescale of the material, such as the structural relaxation time. The degree of supercooling observed in most glassy materials is then set by the typical duration of an experiment, which corresponds to an intrinsic timescale of about 100 s in molecular liquids.

It has recently become possible to prepare “ultrastable” glasses (Swallen et al. 2007; Ediger 2017), namely glassy materials which reach a degree of supercooling which is equivalent to cooling glasses at rates that are 10^5 – 10^{10} times slower than usual. Ultrastable glasses are not prepared by cooling bulk liquids across the glass transition, but using a completely different route called physical vapor deposition. In this procedure, the glassy material is prepared directly at the desired temperature (there is no cooling involved) by the slow deposition of individual molecules suspended in a gas phase onto a glassy film whose height increases slowly as more molecules are deposited.

The degree of supercooling that can be achieved by physical vapor deposition is again set by the competition between two timescales (Swallen et al. 2007; Berthier et al. 2017b). The

extrinsic timescale is now related to the deposition rate of the molecules, whereas the intrinsic timescale is set by the relaxation time of molecules diffusing at the free surface of the glassy film. It is known that bulk and surface dynamics may differ by many orders of magnitude in glasses (Zhu et al. 2011), because the molecular mobility at a free surface is much less constrained than in the bulk. Therefore, for a similar extrinsic timescale imposed by the experimental setup, a much deeper degree of supercooling is achieved by the vapor deposition process.

Ultrastable glasses prepared using physical vapor deposition are thus expected to behave as extraordinarily slowly cooled supercooled liquids, with a cooling rate or a preparation time that is impractically large. As such, these glasses have physical properties that can differ rather drastically from ordinary glassy materials. In particular, it was shown that their mechanical, thermodynamic, and kinetic properties differ quantitatively from ordinary glasses, and display specific dynamic phenomena (Kearns et al. 2010; Chen et al. 2013; Pérez-Castañeda et al. 2014; Sepúlveda et al. 2014; Ràfols-Ribé et al. 2018; Vila-Costa et al. 2020). As such, they are currently the subject of intense theoretical investigations as well (Wolynes 2009; Léonard and Harrowell 2010; Lyubimov et al. 2013; Jack and Berthier 2016; Gutiérrez and Garrahan 2016; Fullerton and Berthier 2017; Flenner et al. 2019; Khomenko et al. 2020). The goal is to better understand the deposition process itself, but also to better characterize the physical properties of ultrastable glasses in view of their many potential practical applications. Also, since ultrastable glasses offer a way to access much deeper supercooled states, it can be hoped that they can be used to shed new light on the glass transition phenomenon itself.

Other Glasses in Physics, and Beyond

There are many other physical contexts in which glassiness plays an important role (Young 1998). One of the most famous examples is the field of spin glasses. Real spin glasses are magnetic impurities interacting by quenched random couplings. At low temperatures, their dynamics become extremely slow and they freeze in amorphous

spin configuration dubbed a “spin glass” by Anderson. There are many other physical systems, often characterized by quenched disorder, that show glassy behavior, like Coulomb glasses, Bose glasses, etc. In many cases, however, one does expect quite a different physics from structural glasses: the similarity between these systems is therefore only qualitative.

Quite remarkably, glassiness also emerges in other branches of science (Bouchaud et al. 2011). In particular, it has been discovered recently that concepts and techniques developed for glassy systems turn out to apply and be very useful tools in the field of computer science. Problems like combinatorial optimization display phenomena completely analogous to phase transitions, and actually, to glassy phase transitions. A posteriori, this is quite natural, because a typical optimization problem consists in finding a solution in a presence of a large number of constraints. This can be defined, for instance, as a set of N Boolean variables that satisfies M constraints. For N and M very large at fixed $\alpha = M/N$, this problem very much resembles finding a ground state in a statistical mechanics problem with quenched disorder. Indeed one can define an energy function (a Hamiltonian) as the number of unsatisfied constraints, that has to be minimized, as in a $T = 0$ statistical mechanics problem. The connection with glassy systems originates from the fact that in both cases the energy landscape is extremely complicated, full of minima and saddles. The fraction of constraints per degree of freedom, α , plays a role similar to the density in a hard sphere system. For instance, a central problem in optimization, random k -satisfiability, has been shown to undergo a glass transition when α increases, analogous to the one of structural glasses (Krzakala et al. 2007; Antenucci et al. 2019).

Glassiness also plays an important role in machine learning and signal processing. In those cases, one wants to learn a specific task from many examples or retrieve a specific signal from a huge amount of data. This is done in practice by minimizing a cost function. For example, imagine that one is given a tensor $T_{i_1, i_2, i_3} = v_{i_1} v_{i_2} v_{i_3}$, constructed from a vector $v_i (i = 1, \dots, N)$ of norm $\sqrt{N}$, and that this tensor is corrupted by

noise J_{i_1, i_2, i_3} , which for simplicity we take independent and Gaussian for each triple (i_1, i_2, i_3) . The problem called tensor PCA, which appears in image and video analysis (Anandkumar et al. 2014), consists in retrieving the signal v_i from the noisy tensor $T_{i_1, i_2, i_3} + J_{i_1, i_2, i_3}$. The simplest procedure to solve this problem is to find the vector x_i minimizing the following cost function:

$$H(\{x_i\}) = \sum_{i_1, i_2, i_3} (v_{i_1} v_{i_2} v_{i_3} + J_{i_1, i_2, i_3} - x_{i_1} x_{i_2} x_{i_3})^2.$$

By developing the square, one finds that the cost function H is identical to the one of a 3-spin spherical glass mean-field model with quenched random couplings J_{i_1, i_2, i_3} and a term favoring configurations in the direction of v_i (Richard and Montanari 2014). These two contributions are competing for determining the ground-state properties, the strength of the latter with respect to the former is proportional to the signal-to-noise ratio. This example illustrates one way in which glassiness plays an important role in machine learning: one has to find a signal (the v_i 's) buried in a rough landscape (induced by the J_{i_1, i_2, i_3} 's). Practical algorithms, such as gradient descent and its stochastic version, lead to dynamics which are very similar to the ones of physical systems after a quench to low temperature. One of the main questions in this area is characterizing the algorithmic threshold, that is, the critical value of the signal-to-noise ratio such that the original signal can be recovered with some given accuracy. Glassy dynamics plays a central role: it is the main obstacle for recovering the signal, as the dynamics can be lost and trapped in bad minima instead of converging toward the good one correlated with the signal (Mannelli et al. 2020).

Finally, hunting for a signal in a rough landscape (Zdeborová and Krzakala 2016) is not the only context in which glassiness emerged in machine learning in recent years. In fact, more generally, there has been a lot of work aimed at characterizing the landscapes over which optimization dynamics take places in general machine learning problems (from high-dimensional statistics to deep neural networks), and at assessing to which extent glassy dynamics and rough

landscapes play a relevant role (Sagun et al. 2014; Baity-Jesi et al. 2019).

Numerical Simulations

Studying the glass transition of molecular liquids at a microscopic level is in principle straightforward since one must answer a very simple question: how do particles move in a liquid close to T_g ? It is of course a daunting task to attempt answering this question experimentally because one should then resolve the dynamics of single molecules to be able to follow the trajectories of objects that are a few Angstroms large on timescales of tens or hundreds of seconds, which sounds like eternity when compared to typical molecular dynamics usually lying in the picosecond regime. In recent years, such direct experimental investigations have been developed using time and space resolved techniques such as atomic force microscopy (Russell and Israeloff 2000) or single molecule spectroscopy (Adhikari et al. 2007; Paeng et al. 2015), but this remains a very difficult task.

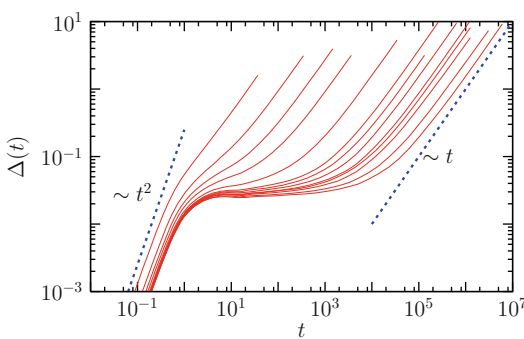
In numerical simulations, by contrast, the trajectory of each particle in the system can, by construction, be followed at all times. This allows one to quantify easily single particle dynamics, as proved in Fig. 4 where the averaged mean-

squared displacement $\Delta(t)$ measured in a simple Lennard-Jones glass-former is shown and is defined as.

$$\Delta(t) = \left\langle \frac{1}{N} \sum_{i=1}^N |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \right\rangle, \quad (6)$$

where $\mathbf{r}_i(t)$ represents the position of particle i at time t in a system composed of N particles and the brackets indicate an ensemble average. The particle displacements considerably slow down when T is decreased and the self-diffusion constant decreases by orders of magnitude, mirroring the behavior of the viscosity shown in Fig. 1 for real systems. Moreover, a rich dynamics is observed, with a plateau regime at intermediate timescales, corresponding to an extended time window during which particles vibrate around their initial positions, exactly as in a crystalline solid. The difference with a crystal is of course that this localization is only transient, and all particles eventually escape and diffuse at long times with a diffusion constant D_s , so that $\Delta(t) \sim 6D_s t$ when $t \rightarrow \infty$.

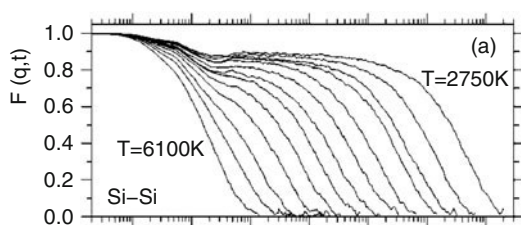
In recent years, computer experiments have played an increasingly important role in glass transition studies. It could almost be said that particle trajectories in numerical work have been studied under so many different angles that probably very little remains to be learned from such studies in the regime that is presently accessible using present day computers. Unfortunately, this does not imply complete knowledge of the physics of supercooled liquids. As shown in Fig. 4, it is presently possible to follow the dynamics of a simple glass-forming liquid over more than eight decades of time, and over a temperature window in which average relaxation timescales increase by more than five decades. This might sound impressive, but a quick look at Fig. 1 shows, however, that at the lowest temperatures studied in the computer, the relaxation timescales are still orders of magnitude faster than in experiments performed close to the glass transition temperature. They can be directly compared to experiments performed in this high temperature regime, but this also implies that simulations



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 4 Mean-squared displacements of individual particles in a simple model of a glass-forming liquid composed of Lennard-Jones particles observed on a wide time window. When temperature decreases (from left to right), the particle displacements become increasingly slow with several distinct time regimes corresponding to (in this order) ballistic, localized, and diffusive regimes

focus on a relaxation regime that is about eight to ten decades of times faster than in experiments performed close to T_g . Whether numerical works are useful to understand the kinetics of the glass transition itself at all is therefore an open, widely debated, question. We believe that it is now possible to numerically access temperatures which are low enough that many features associated to the glass transition physics can be observed: strong decoupling phenomena, clear deviations from fits to the mode-coupling theory (which are experimentally known to hold only at high temperatures), and crossovers toward truly activated dynamics. In section “[New Computational Methods](#),” we discuss recent developments in the field of computational studies that are able to address novel challenges regarding the static properties of supercooled liquids over a broad temperature range.

Classical computer simulations of supercooled liquids usually proceed by solving a cleverly discretized version of Newton’s equations for a given potential interaction between particles (Allen and Tildesley 1989). If quantitative agreement with experimental data on an existing specific material is sought, the interaction must be carefully chosen in order to reproduce reality, for instance by combining classical to **ab initio** simulations. From a more fundamental perspective one rather seeks the simplest model that is still able to reproduce qualitatively the phenomenology of real glass-formers, while being considerably simpler to study. The implicit, but quite strong, hypothesis is that molecular details are not needed to explain the behavior of supercooled liquids, so that the glass transition is indeed a topic for statistical mechanics, not for chemistry. A considerable amount of work has therefore been dedicated to studying models such as hard spheres, soft spheres, or Lennard-Jones particles. More realistic materials are also studied focusing for instance on the physics of network forming materials, multicomponent ones, anisotropic particles, or molecules with internal degrees of freedom. Connections to experimental work can be made by computing quantities that are experimentally accessible such as the intermediate scattering function, static structure factors, $S(\mathbf{q})$, or



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 5 Intermediate scattering function at wavevector $1.7 \text{ \AA}^{-1}$ for the Si particles at $T = 2750 \text{ K}$ obtained from molecular dynamics simulations of a model for silica (Horbach and Kob 2001)

thermodynamic quantities such as specific heat or configurational entropy, which are directly obtained from particle trajectories and can be measured in experiments as well. As an example we show in Fig. 5 the intermediate scattering function $F(\mathbf{q}, t)$ obtained from a molecular dynamics simulation of a classical model for SiO_2 as a function of time for different temperatures (Horbach and Kob 2001).

An important role is played by simulations also because a large variety of dynamic and static quantities can be simultaneously measured in a single model system. As we shall discuss below, there are scores of different theoretical approaches to describe the physics of glass-formers, and sometimes they have their own set of predictions that can be readily tested by numerical work. Indeed, quite a large amount of numerical papers have been dedicated to testing in detail the predictions formulated by the mode-coupling theory of the glass transition, as reviewed in Götze (1999). Here, computer simulations are particularly well-suited as the theory specifically addresses the relatively high temperature window that is studied in computer simulations.

While Newtonian dynamics is mainly used in numerical work on supercooled liquids, a most appropriate choice for these materials, it can be interesting to consider alternative dynamics that are not deterministic, or which do not conserve the energy. In colloidal glasses and physical gels, for instance, particles undergo Brownian motion arising from collisions with molecules in the solvent, and a stochastic dynamics is more appropriate. Theoretical considerations might also suggest

the study of different sorts of dynamics for a given interaction between particles, for instance, to assess the role of conservation laws and structural information. Of course, if a given dynamics satisfies detailed balance with respect to the Boltzmann distribution, all structural quantities remain unchanged, but the resulting dynamical behavior might be very different. Several papers (Gleim et al. 1998; Szamel and Flenner 2004; Berthier and Kob 2007) have studied in detail the influence of the chosen microscopic dynamics on the dynamical behavior in glass-formers using either stochastic dynamics (where a friction term and a random noise are added to Newton's equations, the amplitude of both terms being related by a fluctuation-dissipation theorem), Brownian dynamics (in which there are no momenta, and positions evolve with Langevin dynamics), or Monte-Carlo dynamics (where the potential energy between two configurations is used to accept or reject a trial move). Quite surprisingly, the equivalence between these three types of stochastic dynamics and the originally studied Newtonian dynamics was established at the level of the averaged dynamical behavior (Gleim et al. 1998; Szamel and Flenner 2004; Berthier and Kob 2007), except at very short times where obvious differences are indeed expected. This strongly suggests that an explanation for the appearance of slow dynamics in these materials originates from their amorphous structure. However, important differences were found when dynamic fluctuations were considered (Berthier and Kob 2007; Berthier et al. 2007a, b), even in the long-time regime comprising the structural relaxation.

Another crucial advantage of molecular simulations is illustrated in Fig. 6. This figure shows a spatial map of single particle displacements recorded during the simulation of a binary soft sphere system in two dimensions (Hurley and Harrowell 1995). This type of measurement, out of reach of most experimental techniques that study the liquid state, reveals that dynamics might be very different from one particle to another. More importantly, Fig. 6 also unambiguously reveals the existence of spatial correlations between these dynamic fluctuations. The presence of nontrivial spatiotemporal fluctuations in

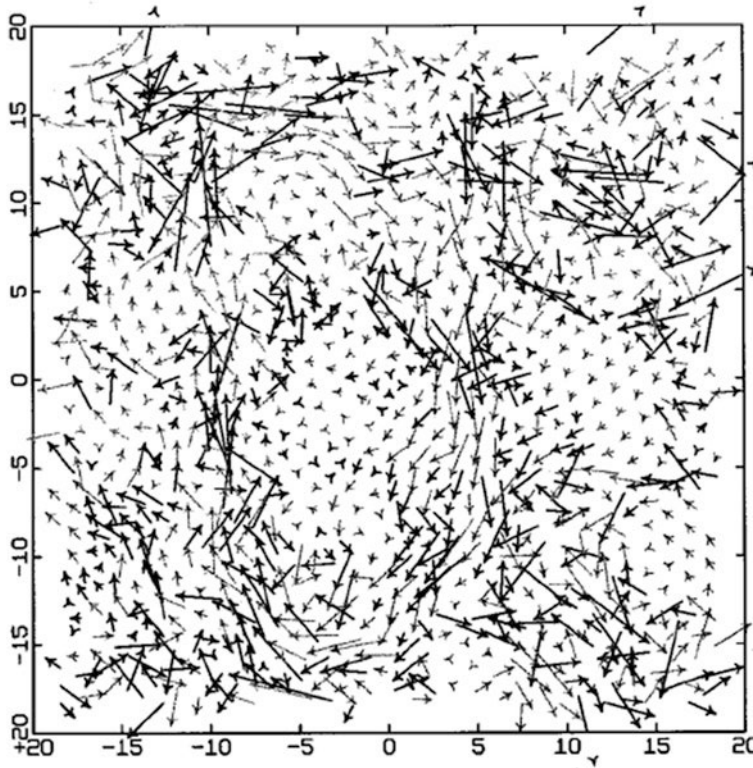
supercooled liquids is now called “dynamic heterogeneity” (Ediger 2000), as we now discuss.

Dynamic Heterogeneity

Existence of Spatiotemporal Dynamic Fluctuations

A new facet of the relaxational behavior of supercooled liquids has emerged in the last two decades thanks to a considerable experimental and theoretical effort. It is called “dynamic heterogeneity” (DH), and now plays a central role in modern descriptions of glassy liquids (Ediger 2000; Berthier et al. 2011a). As anticipated in the previous section, the phenomenon of dynamic heterogeneity is related to the spatiotemporal fluctuations of the dynamics. Initial motivations stemmed from the search of an explanation for the non-exponential nature of relaxation processes in supercooled liquids, related to the existence of a broad relaxation spectrum. Two natural but fundamentally different explanations can be put forward. (1) The relaxation is locally exponential, but the typical relaxation timescale varies spatially. Hence, global correlation or response functions become non-exponential upon spatial averaging over this spatial distribution of relaxation times. (2) The relaxation is complicated and inherently non-exponential, even locally. Experimental and theoretical works (Ediger 2000) suggest that both mechanisms are likely at play, but definitely conclude that relaxation is spatially heterogeneous, with regions that are faster and slower than the average. Since supercooled liquids are ergodic materials, a slow region will eventually become fast, and vice versa. A physical characterization of DH entails the determination of the typical lifetime of the heterogeneities, as well as their typical lengthscale.

A clear and more direct confirmation of the heterogeneous character of the dynamics also stems from simulation studies. For example, whereas the simulated average mean-squared displacements are smooth functions of time, time signals for individual particles clearly exhibit specific features that are not observed unless dynamics is resolved both in space and time. These features



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 6 Spatial map of single particle displacements in the simulation of a binary mixture of soft spheres in two dimensions (Hurley and Harrowell 1995). Arrows show the displacement of each particle in a trajectory of

length about 10 times the structural relaxation time. The map reveals the existence of particles with different mobilities during relaxation, but also the existence of spatial correlations between these dynamic fluctuations

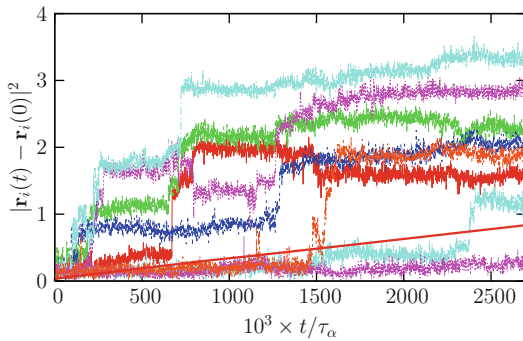
are displayed in Fig. 7. What do we see? We mainly observe that particle trajectories are not smooth but rather composed of a succession of long periods of time where particles simply vibrate around well-defined locations, separated by rapid “jumps.” Vibrations were previously inferred from the plateau observed at intermediate times in the mean-squared displacements of Fig. 4, but the existence of jumps that are clearly statistically widely distributed in time cannot be guessed from averaged quantities only. The fluctuations in Fig. 7 suggest, and direct measurements confirm, the importance played by fluctuations around the averaged dynamical behavior.

A simple type of such fluctuations has been studied in much detail. When looking at Fig. 7, it is indeed natural to ask, for any given time, what is the distribution of particle displacements. This

is quantified by the self-part of the van-Hove function defined as

$$G_s(\mathbf{r}, t) = \left\langle \frac{1}{N} \sum_{i=1}^N \delta(\mathbf{r} - [\mathbf{r}_i(t) - \mathbf{r}_i(0)]) \right\rangle. \quad (7)$$

For an isotropic Gaussian diffusive process, one gets $G_s(\mathbf{r}, t) = \exp(-|\mathbf{r}|^2/(4D_s t))/(4\pi D_s t)^{3/2}$. Simulations reveal instead strong deviations from Gaussian behavior on the timescales relevant for structural relaxation (Kob et al. 1997). In particular they reveal “fat” tails in the distributions that are much wider than expected from the Gaussian approximation. These tails are in fact better described by an exponential decay rather than a Gaussian one, in a wide time window comprising the structural relaxation, such that



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 7 Time resolved squared displacements of individual particles in a simple model of a glass-forming liquid composed of Lennard-Jones particles. The average is shown as a smooth full line. Trajectories are composed of long periods of time during which particles vibrate around well-defined positions, separated by rapid jumps that are widely distributed in time, underlying the importance of dynamic fluctuations

$G_s(\mathbf{r}, t) \sim \exp(-|\mathbf{r}|/\lambda(t))$ (Chaudhuri et al. 2007). Thus, they reflect the existence of a population of particles that moves distinctively further than the rest and appears therefore to be much more mobile. This observation implies that relaxation in a viscous liquid qualitatively differs from that of a normal liquid where diffusion is close to Gaussian, and that a nontrivial single particle displacements statistics exists.

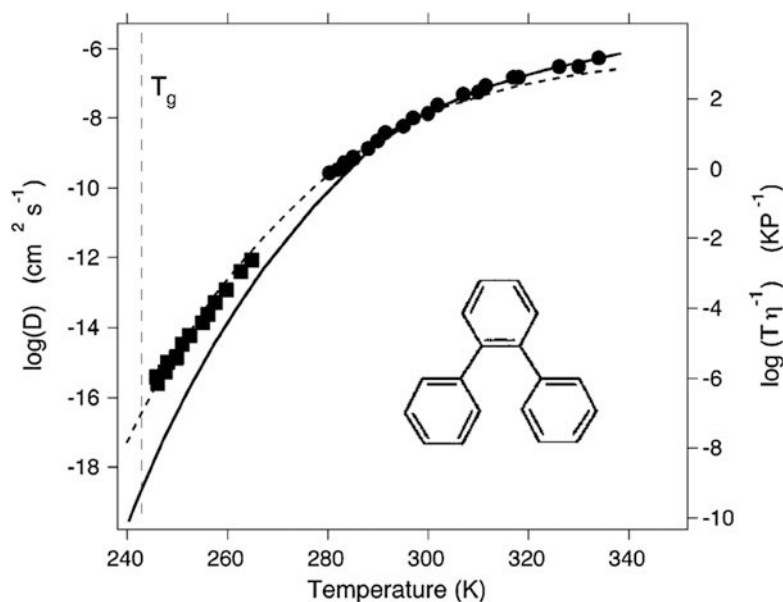
A long series of questions immediately follows this seemingly simple observation. Answering them has been the main occupation of many workers in this field over the last decade. What are the particles in the tails effectively doing? Why are they faster than the rest? Are they located randomly in space or do they cluster? What is the geometry, time, and temperature evolution of the clusters? Are these spatial fluctuations correlated to geometric or thermodynamic properties of the liquids? Do similar correlations occur in all glassy materials? Can one predict these fluctuations theoretically? Can one understand glassy phenomenology using fluctuation-based arguments? Can these fluctuations be detected experimentally?

Another influential phenomenon that was related early on to the existence of DH is the decoupling of self-diffusion (D_s) and viscosity (η). In the high temperature liquid self-diffusion

and viscosity are related by the Stokes-Einstein relation (Hansen and McDonald 1990), $D_s\eta/T = \text{const.}$ For a large particle moving in a fluid the constant is equal to $1/(6\pi R)$ where R is the particle radius. Physically, the Stokes-Einstein relation means that two different measures of the relaxation time R^2/D_s and $\eta R^3/T$ lead to the same time-scale up to a constant factor. In supercooled liquids this phenomenological law breaks down, as shown in Fig. 8 for ortho-terphenyl (Mapes et al. 2006). It is commonly found that D_s^{-1} does not increase as fast as η so that, at T_g , the product $D_s\eta$ has increased by 2–3 orders of magnitude as compared to its Stokes-Einstein value. This phenomenon, although less spectacular than the overall change of viscosity, is a significant indication that different ways to measure relaxation times lead to different answers and thus is a strong hint of the existence of a distribution of relaxation timescales.

Indeed, a natural explanation of this effect is that different observables probe the underlying distribution of relaxation times in different ways (Ediger 2000). For example, the self-diffusion coefficient of tracer particles is dominated by the more mobile particles whereas the viscosity or other measures of structural relaxation probe the timescale needed for every particle to move. An unrealistic but instructive example is a model where there is a small, non-percolative subset of particles that are blocked forever, coexisting with a majority of mobile particles. In this case, the structure never relaxes but the self-diffusion coefficient is nonzero because of the mobile particles. Of course, in reality all particles move, eventually, but this shows how different observables are likely to probe different moments of the distribution of timescales, as explicitly shown within several theoretical frameworks (Tarjus and Kivelson 1995; Jung et al. 2004).

The phenomena described above, although certainly an indication of spatiotemporal fluctuations, do not allow one to study how these fluctuations are correlated in space. This is however a fundamental issue both from the experimental and theoretical points of view. How large are the regions that are faster or slower than the average? How does their size depend on temperature? Are



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 8 Decoupling between viscosity (full line) and self-diffusion coefficient (symbols) in supercooled

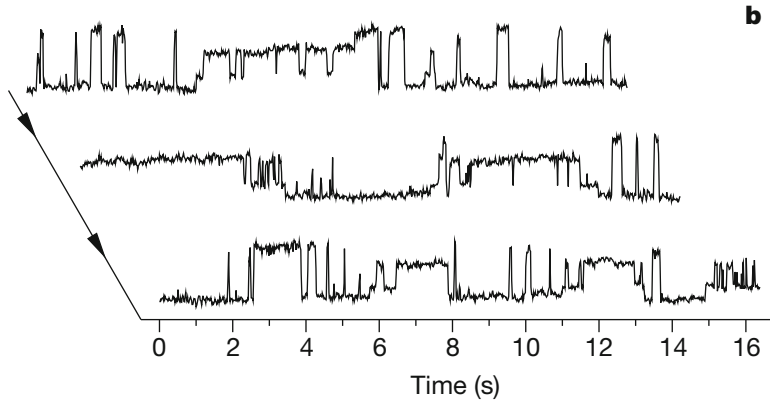
ortho-terphenyl (Mapes et al. 2006). The dashed line shows a fit with a “fractional” Stokes-Einstein relation, $D_s \sim (T/\eta)^\zeta$ with $\zeta \sim 0.82$

these regions compact or fractal? These important questions were first addressed in pioneering works using four-dimensional NMR (Reinsberg et al. 2001), or by directly probing fluctuations at the nanoscopic scale using microscopy techniques. In particular, Vidal Russel and Israeloff using Atomic Force Microscopy techniques (Russell and Israeloff 2000) measured the polarization fluctuations in a volume of size of few tens of nanometers in a supercooled polymeric liquid (PVAc) close to T_g . In this spatially resolved measurement, the hope is to probe a small enough number of dynamically correlated regions, and detect their dynamics. Indeed, the signal shown in Fig. 9 shows a dynamics which is very intermittent in time, switching between periods with intense activity and other periods with no dynamics at all, suggesting that extended regions of space indeed transiently behave as fast or slow regions. A much smoother signal would be measured if such dynamically correlated “domains” were not present. Spatially resolved and NMR experiments are quite difficult. They give undisputed information about the typical lifetime of the DH, but their determination of a dynamic

correlation lengthscale is rather indirect and/or performed on a small number of liquids in a small temperature window. Nevertheless, the outcome is that a nontrivial dynamic correlation length emerges at the glass transition, where it reaches a value of the order of 5–10 molecule diameters (Ediger 2000).

Multipoint Correlation Functions

More recently, substantial progress in characterizing spatiotemporal dynamical fluctuations was obtained from theoretical (Berthier et al. 2007a, b; Franz and Parisi 2000; Toninelli et al. 2005) and numerical results (Hurley and Harrowell 1995; Yamamoto and Onuki 1998; Franz et al. 1999; Bennemann et al. 1999; Lačević et al. 2003; Berthier 2004). In particular, it is now understood that dynamical fluctuations can be measured and characterized through the use of four-point correlation functions. These multipoint functions can be seen as a generalization of the spin glass susceptibility measuring the extent of amorphous long-range order in spin glasses. In this subsection, we introduce these correlation functions and summarize the main results obtained using them.



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 9 Time series of polarization in the AFM experiment performed by Vidal Russell and Israeloff (2000) on PVAc at $T = 300$ K. The signal intermittently

switches between periods with fast or slow dynamics, suggesting that extended regions of space indeed transiently behave as fast and slow regions

Standard experimental probes of the averaged dynamics of liquids give access to the time-dependent autocorrelation function of the spontaneous fluctuations of some observable $O(t)$, $F(t) = \langle \delta O(0) \delta O(t) \rangle$, where $\delta O(t) = O(t) - \langle O \rangle$ represents the instantaneous value of the deviation of $O(t)$ from its ensemble average $\langle O \rangle$ at time t . One can think of $F(t)$ as being the average of a two-point quantity, $C(0, t) = \delta O(0) \delta O(t)$, characterizing the dynamics. A standard example corresponds to O being equal to the Fourier transform of the density field. In this case $F(t)$ is the dynamical structure factor as in Eq. (5). More generally, a correlation function $F(t)$ measures the global relaxation in the system. Intuitively, in a system with important dynamic correlations, the fluctuations of $C(0, t)$ are stronger. Quantitative information on the amplitude of those fluctuations is provided by the variance

$$\chi_4(t) = N \langle \delta C(0, t)^2 \rangle, \quad (8)$$

where $\delta C(0, t) = C(0, t) - F(t)$, and N is the total number of particles in the system. The associated spatial correlations show up more clearly when considering a “local” probe of the dynamics, like for instance an orientational correlation function measured by dielectric or light scattering experiments, which can be expressed as

$$C(0, t) = \frac{1}{V} \int d^3r c(\mathbf{r}; 0, t), \quad (9)$$

where V is the volume of the sample and $c(\mathbf{r}; 0, t)$ characterizes the dynamics between times 0 and t around point $\mathbf{r}$. For example, in the above mentioned case of orientational correlations, $c(\mathbf{r}; 0, t) \propto \frac{1}{N} \sum_{i,j=1}^N \delta(\mathbf{r} - \mathbf{r}_i) Y(\Omega_i(0)) Y(\Omega_j(t))$, where Ω_i denotes the angles describing the orientation of molecule i , $\mathbf{r}_i(0)$ is the position of that molecule at time 0, and $Y(\Omega)$ is some appropriate rotation matrix element. Here, the “locality” of the probe comes from the fact that it is dominated by the self-term involving the same molecule at times 0 and t , or by the contribution coming from neighboring molecules. The dynamic susceptibility $\chi_4(t)$ can thus be rewritten as

$$\chi_4(t) = \rho \int d^3r G_4(\mathbf{r}; 0, t), \quad (10)$$

where

$$G_4(\mathbf{r}; 0, t) = \langle \delta c(\mathbf{0}; 0, t) \delta c(\mathbf{r}; 0, t) \rangle, \quad (11)$$

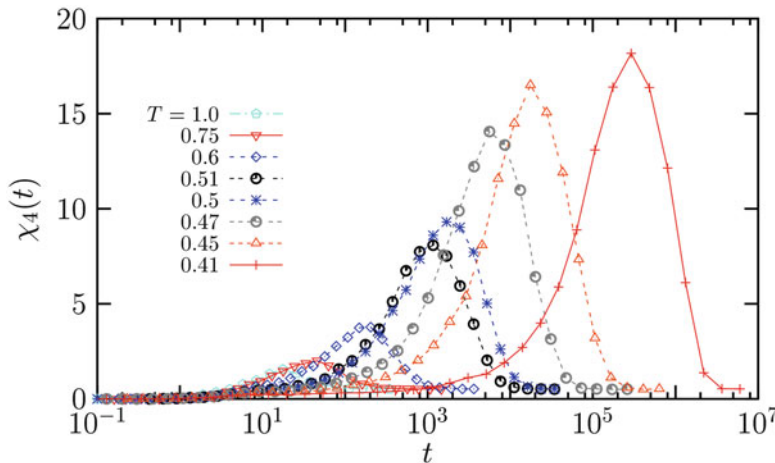
and translational invariance has been taken into account ($\rho = N/V$ denotes the mean density). The above equations show that $\chi_4(t)$ measures the extent of spatial correlation between dynamical

events at times 0 and t at different points, that is, the spatial extent of dynamically heterogeneous regions over a time span t .

The function $\chi_4(t)$ has been measured by molecular dynamics, Brownian and Monte Carlo simulations in different liquids (Franz et al. 1999; Bennemann et al. 1999; Lačević et al. 2003; Berthier 2004, 2007a; Gebremichael et al. 2004). An example is shown in Fig. 10 for a Lennard-Jones liquid. The qualitative behavior is similar in all cases (Berthier et al. 2007a; Franz and Parisi 2000; Toninelli et al. 2005): as a function of time $\chi_4(t)$ first increases, it has a peak on a timescale that tracks the structural relaxation timescale and then it decreases. (The decrease at long times constitutes a major difference with spin glasses. In a spin glass, χ_4 would be a monotonically increasing function of time whose longtime limit coincides with the static spin glass susceptibility. Physically, the difference is that spin glasses develop long-range static amorphous order while structural glasses do not or, at least, in a different and more subtle way.) Thus the peak value measures the volume on which the structural relaxation processes are correlated. It is found to increase when the temperature decreases and the dynamics slows down. By measuring directly $G_4(\mathbf{r}; 0, t)$ it has also been checked that the increase of the peak of $\chi_4(t)$ corresponds, as

expected, to a growing dynamic lengthscale ξ (Berthier et al. 2007a; Bennemann et al. 1999; Lačević et al. 2003; Berthier 2004), although these measurements are much harder in computer simulations, because very large systems need to be simulated to determine ξ unambiguously. Note that if the dynamically correlated regions were compact, the peak of χ_4 would be proportional to ξ^3 in three dimensions, directly relating χ_4 measurements to that of the relevant lengthscale of DH.

These results are also relevant because many theories of the glass transition assume or predict, in a way or another, that the dynamics slows down because there are increasingly large regions on which particles have to relax in a correlated or cooperative way. However, this lengthscale remained elusive for a long time. Measures of the spatial extent of dynamic heterogeneity, in particular $\chi_4(t)$ and $G_4(\mathbf{r}; 0, t)$, seem to provide the long-sought evidence of this phenomenon. This in turn suggests that the glass transition is indeed a critical phenomenon characterized by growing timescales and lengthscales. A clear and conclusive understanding of the relationship between the lengthscale obtained from $G_4(\mathbf{r}; 0, t)$ and the relaxation timescale is still the focus of an intense research activity.



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 10 Time dependence of $\chi_4(t)$, quantifying the spontaneous fluctuations of the intermediate scattering function in a Lennard-Jones supercooled liquid. For each

temperature, $\chi_4(t)$ has a maximum, which shifts to larger times and has a larger value when T is decreased, revealing the increasing lengthscale of dynamic heterogeneity in supercooled liquids approaching the glass transition

One major issue is that obtaining information on the behavior of $\chi_4(t)$ and $G_4(\mathbf{r}; 0, t)$ from experiments is difficult. Such measurements are necessary because numerical simulations can only be performed rather far from T_g , see section “[Numerical Simulations](#).” Up to now, direct experimental measurements of $\chi_4(t)$ have been restricted to colloidal (Weeks et al. 2007) and granular materials (Keys et al. 2007; Dauchot et al. 2005) close to the jamming transition, because dynamics is more easily spatially resolved in those cases. Unfortunately, similar measurements are currently not available in molecular liquids.

Recently, an approach based on fluctuation-dissipation relations and rigorous inequalities has been developed in order to overcome this difficulty (Berthier et al. 2005, 2007a; b; Dalle-Ferrier et al. 2007). The main idea is to obtain a rigorous lower bound on $\chi_4(t)$ using the Cauchy-Schwarz inequality $\langle \delta H(0) \delta C(0, t) \rangle^2 \leq \langle \delta H(0)^2 \rangle \langle \delta C(0, t)^2 \rangle$, where $H(t)$ denotes the enthalpy at time t . By using fluctuation-dissipation relations the previous inequality can be rewritten as (Berthier et al. 2005)

$$\chi_4(t) \geq \frac{k_B T^2}{c_P} [\chi_T(t)]^2, \quad (12)$$

where the multipoint response function $\chi_T(t)$ is defined by

$$\begin{aligned} \chi_T(t) &= \left. \frac{\partial F(t)}{\partial T} \right|_{N,P} \\ &= \frac{N}{k_B T^2} \langle \delta H(0) \delta C(0, t) \rangle. \end{aligned} \quad (13)$$

In this way, the experimentally accessible response $\chi_T(t)$ which quantifies the sensitivity of average correlation functions $F(t)$ to an infinitesimal temperature change, can be used in Eq. (12) to yield a lower bound on $\chi_4(t)$. Moreover, detailed numerical simulations and theoretical arguments (Berthier et al. 2007a, b) strongly suggest that the right hand side of (12) actually provides a good estimation of $\chi_4(t)$, not just a lower bound.

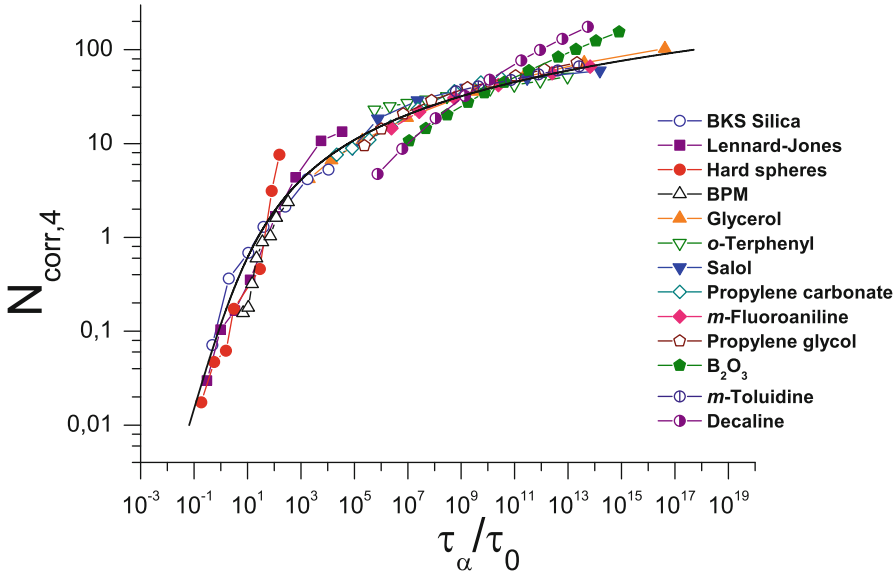
Using this method, Dalle-Ferrier et al. (2007) have been able to obtain the evolution of the peak

value of χ_4 for many different glass-formers in the entire supercooled regime. In Fig. 11 we show some of these results as a function of the relaxation timescale. The value on the y -axis, the peak of χ_4 , is a proxy for the number of molecules, $N_{\text{corr},4}$ that have to evolve in a correlated way in order to relax the structure of the liquid. Note that χ_4 is expected to be equal to $N_{\text{corr},4}$ only up to a proportionality constant that is not known from experiments, which probably explains why the high temperature values of $N_{\text{corr},4}$ are smaller than one. Figure 11 also indicates that $N_{\text{corr},4}$ grows faster when T_α is not very large, close to the onset of slow dynamics, and a power law relationship between $N_{\text{corr},4}$ and T_α fits this regime well ($\tau_\alpha/\tau_0 < 10^4$). The growth of $N_{\text{corr},4}$ becomes much slower closer to T_g . A change of six decades in time corresponds to a mere increase of a factor about 4 of $N_{\text{corr},4}$, suggesting logarithmic rather than power law growth of dynamic correlations. This is in agreement with several theories of the glass transition which are based on activated dynamic scaling (Xia and Wolynes 2000; Garrahan and Chandler 2003; Tarjus et al. 2005).

Understanding quantitatively this relation between timescales and lengthscales is one of the main recent topics addressed in theories of the glass transition, see section “[Theory of the Glass Transition](#).” Furthermore, numerical works are also devoted to characterizing better the geometry of the dynamically heterogeneous regions (Donati et al. 1998; Appignanesi et al. 2006; Kob et al. 2012).

Nonlinear Response Function

Diverging responses are characteristic signatures of phase transitions. Linear static responses measuring the change in the order parameter due to external fields diverge at second-order phase transitions (Chaikin et al. 1995). By using fluctuation-dissipation relations one can show that such divergence is intimately related to the divergence of the correlation length emerging in two point-functions. Spin-glasses, the archetypal example of disordered systems, display a diverging static magnetic nonlinear cubic response (Binder and Young 1986; Baity-Jesi et al. 2013). In Bouchaud and Biroli (2005) it was argued that the



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 11 Universal dynamic scaling relation between number of dynamically correlated particles,

$N_{\text{corr},4}$, and relaxation timescale, τ_α , for a number of glass-formers (Dalle-Ferrier et al. 2007), determined using Eq. (12)

counterpart of these phenomena for supercooled liquids can be found in nonlinear dynamical susceptibilities, which should grow approaching the glass transition, thus providing a complementary way (compared to χ_4) to reveal its collective nature. In experiments on molecular liquids, nonlinear dielectric susceptibility is a natural probe to unveil this phenomenon.

The simplest explanation (Albert et al. 2016) for this scenario is based on the assumption that $N_{\text{corr}} = (\ell/a)^{d_f}$ molecules are amorphously ordered over the lengthscale ℓ , where a is the molecular size and d_f is the fractal dimension of the ordered clusters. In consequence, their dipoles, which are oriented in apparently random positions, are essentially locked together during a time τ_α . In the presence of an external electric field E oscillating at frequency $\omega \geq \tau_\alpha^{-1}$, the dipolar degrees of freedom of these molecules contribute to the polarization per unit volume as

$$p = \mu_{\text{dip}} \frac{\sqrt{(\ell/a)^{d_f}}}{(\ell/a)^d} F\left(\frac{\mu_{\text{dip}} E \sqrt{(\ell/a)^{d_f}}}{kT}\right) \quad (14)$$

where μ_{dip} is an elementary dipole moment, F is an odd scaling function, and $d = 3$ the dimension

of space. This states that randomly locked dipoles have an overall moment $\sqrt{N_{\text{corr}}}$, and that we should compare the thermal energy with the energy of this “super-dipole” in a field.

Expanding Eq. 14 in powers of E , one finds the “glassy” contribution to p :

$$\begin{aligned} \frac{p}{\mu_{\text{dip}}} &= F'(0) \left(\frac{\ell}{a}\right)^{d_f-d} \left(\frac{\mu_{\text{dip}} E}{kT}\right) + \\ &+ \frac{1}{3!} F^{(3)}(0) \left(\frac{\ell}{a}\right)^{2d_f-d} \left(\frac{\mu_{\text{dip}} E}{kT}\right)^3 + \quad (15) \\ &+ \frac{1}{5!} F^{(5)}(0) \left(\frac{\ell}{a}\right)^{3d_f-d} \left(\frac{\mu_{\text{dip}} E}{kT}\right)^5 + \dots \end{aligned}$$

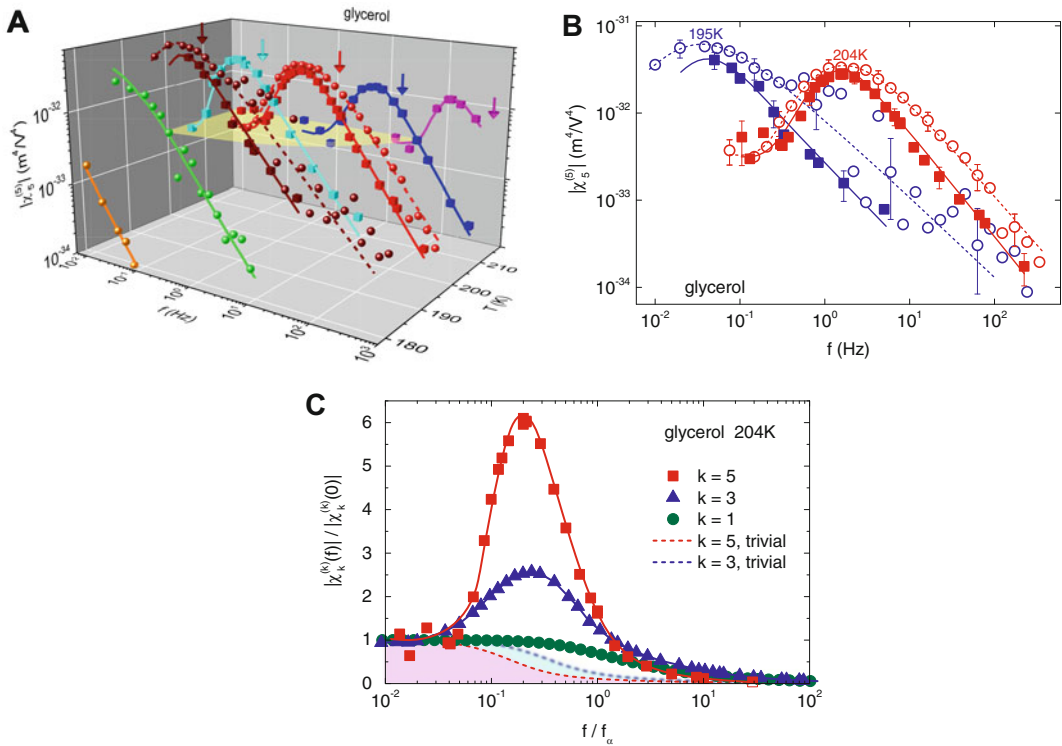
Because $d_f \leq d$, the first term, contributing to the usual linear dielectric susceptibility, $\chi_1(\omega)$, cannot grow as ℓ increases. This simple theoretical argument explains why spatial glassy correlations does not show up in $\chi_1(\omega)$, in experiments. The second term, contributing to the third-order dielectric susceptibility $\chi_3(\omega)$, does grow with ℓ provided $d_f > d/2$. Several theories indeed suggest that ordered domains are compact, $d_f = d$ (Tarjus et al. 2005; Wolynes and Lubchenko 2012). The third term leads to the fifth-order susceptibility $\chi_5(\omega)$, which should diverge as ℓ^{3d_f-d} (higher

n -order susceptibilities diverge as $\ell^{(n+1)d_f/2-d}$. This line of arguments shows that measuring non-linear susceptibilities is a way to probe and characterize the collective dynamical behavior associated to glassy dynamics.

This challenge was taken up in the series of works (Albert et al. 2016; Crauste-Thibierge et al. 2010; Bauer et al. 2013; Brun et al. 2012). The main outcomes of these experiments have been: (i) to show that indeed a growth of the nonlinear responses goes along with the glass transition, (ii) to measure in a new way the number of correlated molecules close to T_g , (iii) to estimate that $d_f \simeq d$ (for $d = 3$). As an example, we reproduce the results of (Albert et al. 2016) in Fig. 12, which shows the increase of the fifth-order susceptibility with temperature (panel A), its humped shape in frequency

(panel B), and the stronger singularity of the fifth-order susceptibility compared to the third-order one (panel C), as expected for a collective phenomenon.

Another set of experiments on nonlinear responses was performed in colloids: nonlinear mechanical susceptibilities were probed approaching the colloidal glass transition (Seyboldt et al. 2016) and shown to grow approaching it. Differently from the dielectric case, third-harmonic shear responses have a peak at a frequency associated to the β -relaxation, and not to the α -relaxation. The reason is related to the fact that a very slow shear-strain does not affect the relaxation time-scale, whereas an external electric field (even a static one) does, see Seyboldt et al. (2016).



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 12 Modulus of the fifth-order susceptibility in supercooled glycerol as a function of frequency (from Albert et al. (2016)). (a) The susceptibilities $\chi_5^{(5)}$ reported are obtained directly by monitoring the response of the sample at 5ω , when applying an electric field E at angular

frequency ω . Two independent setups were used. Lines are guides for the eyes. (b) Projection onto the susceptibility-frequency plane of the data of panel A at 204 K and at 195 K. (c) Comparison of the fifth-order, cubic, and linear susceptibilities. Symbols, with line to guide the eyes. The higher the order k , the stronger the hump of $|\chi_k^{(k)}|$

Finally, a word about theories. Given that the growth of nonlinear dynamical susceptibility is a relatively newly established fact in the glass-physics arena, one can wonder how the different theoretical framework developed to explain the glass transitions cope with it. Thermodynamic theories based on the increases of some kind of medium range order naturally do, as explained above. Mode-Coupling-Theory also predicts diverging dynamical nonlinear susceptibility at the MCT transition (Seyboldt et al. 2016; Tarzia et al. 2010). Purely local theory are instead at odds. Dynamical facilitation theory was argued to be compatible with such findings in Speck (2019), even though the general arguments put forward in Albert et al. (2016) indicate the opposite conclusion.

Theory of the Glass Transition

We now present some theoretical approaches to the glass transition. It is impossible to cover all of them in a brief review, simply because there are way too many of them, perhaps the clearest indication that the glass transition remains an open problem. We choose to present approaches that are keystones and have a solid statistical mechanics basis. Loosely speaking, they have a Hamiltonian, can be simulated numerically, or studied analytically with statistical mechanics tools. Of course, the choice of Hamiltonians is crucial and contains very important assumptions about the nature of the glass transition. All these approaches have given rise to unexpected results. One finds more in them than what was supposed at the beginning, which leads to new, testable predictions. Furthermore, with models that are precise enough, one can test (and hopefully falsify!) these approaches by working out all their predictions in great detail, and comparing the outcome to actual data. This is not possible with “physical pictures,” or simpler approaches of the problem which we therefore do not discuss.

Before going into the models, we would like to state the few important questions that theoreticians face.

- Why do the relaxation time and the viscosity increase when T_g is approached? Why is this growth super-Arrhenius?
- Can one understand and describe quantitatively the average dynamical behavior of supercooled liquids, in particular broad relaxation spectra, non-exponential behavior, and their evolution with fragility?
- Is there a relation between kinetics and thermodynamics (like $T_0 \simeq T_K$), and why?
- Can one understand and describe quantitatively the spatiotemporal fluctuations of the dynamics? How and why are these fluctuations related to the dynamic slowing down?
- Is the glass transition a collective phenomenon? If yes, of which kind? Is there a finite temperature or zero temperature ideal glass transition?
- Is the slowing down of the dynamics driven by the growth of amorphous order and a static length? Or is its origin purely dynamic?
- Is there a geometric, real space explanation for the dynamic slowing down that takes into account molecular degrees of freedom?

The glass transition appears as a kind of “intermediate coupling” problem, since for instance typical growing lengthscales are found to be at most a few tens of particles large close to T_g . It would therefore be difficult to recognize the correct theory even if one bumped into it. To obtain quantitative, testable predictions, one must therefore be able to work out also preasymptotic effects. This is particularly difficult, especially in cases where the asymptotic theory itself has not satisfactorily been worked out. As a consequence, at this time, theories can only be judged by their overall predictive power and their theoretical consistency.

Random First-Order Transition Theory

Mean-Field Models and a Zest of Replica Theory

In the last three decades, three independent lines of research, Adam-Gibbs theory (Adam and Gibbs 1965), mode-coupling theory (Götze 1999), and spin glass theory (Mézard et al. 1987), have merged to produce a theoretical

ensemble that now goes under the name of Random First-Order Transition theory (RFOT), a terminology introduced by Kirkpatrick, Thirumalai, and Wolynes (Kirkpatrick and Thirumalai 1987; Kirkpatrick and Wolynes 1987a) who played a major role in this unification. Instead of following the rambling development of history, we summarize it in a more modern and unified way.

A key ingredient of RFOT theory is the existence of a chaotic or complex free energy landscape with a specific evolution with temperature and/or density. Analyzing it in a controlled way for three-dimensional interacting particles is an impossible task. This can be achieved, however, in simplified models or using mean-field approximations that have therefore played a crucial role in the development of RFOT theory.

A first concrete example is given by “lattice glass models” (Biroli and Mézard 2001). These are models of hard particles sitting on a lattice. The Hamiltonian is infinite either if there is more than one particle on a site or if the number of occupied neighbors of an occupied site is larger than a parameter m , but is zero otherwise. Tuning the parameter m , or changing the type of lattice, in particular its connectivity, yields different models. Lattice glasses are constructed as simple statmech models to study the glassiness of hard sphere systems. The constraint on the number of occupied neighbors mimics the geometric frustration (Nelson 2002) encountered when trying to pack hard spheres in three dimensions. Numerical simulations show that their phenomenological glassy behavior is indeed analogous to the one of supercooled liquids (Darst et al. 2010; Seif and Grigera 2016; Nishikawa and Hukushima 2020). Other models with a finite energy are closer to molecular glass-formers, and can also be constructed (McCullagh et al. 2005). These models can be solved exactly on a Bethe lattice, which reveals a rich physical behavior (Rivoire et al. 2004). (In order to have a well-defined thermodynamics, Bethe lattices are generated as random graphs with fixed connectivity, also called random regular graphs.) In particular their free energy landscape can be analyzed in full details and turns out to have the properties that are also found in several “generalized spin glasses.” Probably the most

studied example of such spin glasses is the p -spin model, defined by the Hamiltonian (Gross and Mézard 1984)

$$H = - \sum_{i_1, \dots, i_p} J_{i_1, \dots, i_p} S_{i_1} \dots S_{i_p}, \quad (16)$$

where the S_i ’s are N Ising or spherical spins, $p > 2$ is the number of interacting spins in a single term of the sum, and $J_{i_1, \dots, i_p}$ quenched random couplings extracted from a distribution which, with no loss of generality, can be taken as the Gaussian distribution with zero mean and variance $p!/(2N^{p-1})$. In this model, the couplings $J_{i_1, \dots, i_p}$ play the role of self-induced disorder in glasses, and promote a glass phase at low temperature.

All these models can be analyzed using the so-called replica theory (Mézaré et al. 1987). Given its importance in setting the foundations of the theory of glasses at the mean-field level, we now present its main technical steps. To keep the discussion as simple as possible, we focus on p -spin models. Note that the theory holds for more complex models but it is technically more involved. The starting point is the computation of the free-energy which is obtained as an average over the distribution of couplings:

$$F = \lim_{N \rightarrow \infty} - \frac{1}{\beta N} \overline{\log Z_J}, \quad (17)$$

where $\overline{}$ represents the average over the disorder. Performing this average is possible thanks to the replica trick

$$\overline{\log Z_J} = \lim_{n \rightarrow 0} \frac{1}{n} \log \overline{Z^n}, \quad (18)$$

where n is the index of replicas, that is, clones of the same system with different couplings $J_{i_1, \dots, i_p}$ extracted from the same distribution. The use of the replica trick may seem purely mathematical, yet it has a profound physical sense. If the system is ergodic, averages of thermodynamical observables for two replicas of the same system (with identical disorder) coincide, whereas they differ if ergodicity is broken. We can define the overlaps

between two replicas a, b as Q_{ab} , which defines the $n \times n$ overlap matrix:

$$Q_{ab} = \frac{1}{N} \sum_{i=1}^N S_i^a S_i^b, \quad (19)$$

where the product between spins represents a dot product for spherical spins (Castellani and Cavagna 2005). After some computations, the free energy can be expressed as a function of Q_{ab} , which therefore plays the role of the order parameter. In the ergodic phase one expects symmetry between replicas (if additional symmetries are broken, then one can have ergodicity breaking also in the RS phase), and the so-called replica-symmetric (RS) parameterization of Q_{ab} is adopted: all the off-diagonal elements of Q_{ab} are equal to $q_0 < 1$ and the diagonal elements are $Q_{aa} = 1$. The parameterization that corresponds to the glass phase, when ergodicity is broken, is the so-called one-step replica symmetry breaking (1RSB) solution. Here, the overlap matrix is divided into blocks of dimension $m \times m$; elements belonging to blocks far from the diagonal are equal to q_0 , while off-diagonal elements of blocks along the diagonal are equal to q_1 with $1 > q_1 > q_0$. On the diagonal $Q_{aa} = 1$. This parameterization encodes the existence of many thermodynamically equivalent basins, hence two replicas can either fall in the same basin and have overlap q_1 , or fall in two different basins and have overlap q_0 . The crucial simplification introduced by the mean-field approximation is that barriers between basins have a free energy cost which grows exponentially with N , so that truly metastable states can be defined in the thermodynamic limit (Cavagna 2009). At high temperature (or low density) the RS solution has a lower free energy. Below the ideal glass transition temperature the 1RSB solution instead becomes dominant.

Liquids and Glasses in Infinite Dimensions

A major theoretical breakthrough of the last years is the analysis of the glass transition for interacting particle systems in the limit of infinite dimensions (Kurchan et al. 2012, 2013; Charbonneau et al. 2014a, b; Parisi et al. 2020). The starting point approach is the definition of a pair interaction

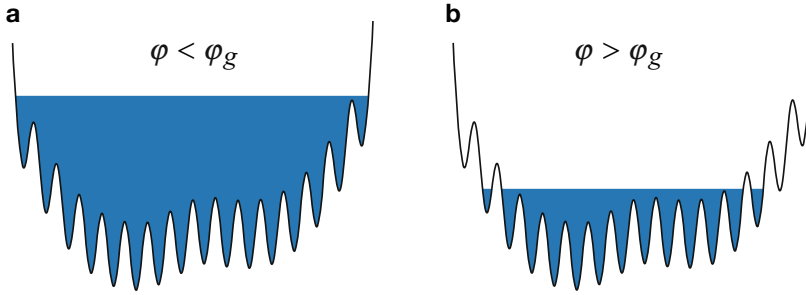
potential with a proper scaling with dimension d to ensure a nontrivial thermodynamic limit:

$$v(r) = \tilde{v}[d(r/\ell - 1)] \quad (20)$$

where ℓ defines the range of the interaction. Many different potentials used to model glasses can be written in this way by using a suitable function $\tilde{v}(x)$, such as hard spheres, Lennard-Jones, Yukawa, square-well, harmonic, and Weeks-Chandler-Andersen potentials (Parisi et al. 2020). In the limit of infinite space dimension, $d \rightarrow \infty$, and using the scaling above, the thermodynamics and the dynamics of liquids and glasses can be analyzed exactly. (For large d the crystalline phase does not intervene. In fact, the amorphous and crystalline solid phases are well separated in configuration space and issues related to finite dimensions, such as the crystallization of monodisperse particles, are suppressed (Skoge et al. 2006; van Meel et al. 2009).) The resulting theory is qualitatively very similar to the one obtained from the simple models discussed in the previous section (both for the statics, in terms of replica formalism, and for the dynamics, in terms of self-consistent Langevin equations).

In fact, all these models belong to the universality class of 1RSB systems (Charbonneau et al. 2014b), with a free-energy landscape evolving as in the sketch in Fig. 13. At low densities or high enough temperatures, they all describe an ergodic liquid phase, analogous to the paramagnetic phase of a spin glass. Under cooling or application of an external pressure, the free energy breaks up into many different minima which eventually trap the dynamics, and the system enters the glass phase, as described further below.

The merit of the infinite dimensional theory is that it offers quantitative results and applies directly to microscopic models of liquids and glasses. Moreover, it directly reveals the nature of “mean-field” theories and approximations, such as the diagrammatic liquid theory and Mode-Coupling Theory. Last but not least, it establishes once and for all that the 1RSB phase and associated physics and phase transition is the correct and universal mean-field theory of glass-forming models.



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 13 Sketch of the evolution of free-energy landscape of hard spheres across the glass transition. In the liquid phase (a) at low packing fractions $\varphi < \varphi_g$, every

portion of the phase space is accessible. For $\varphi > \varphi_g$ the system is in the glass phase (b) and remains trapped in one of the many equivalent basins

Random First-Order Transitions

We now discuss the physics associated to the 1RSB phase transition, and more generally to RFOT. The free energy landscape of glassy systems is “rugged,” as shown in Fig. 13. It is characterized by many minima and saddle points of various orders. Actually, the number of stationary points is so large that in order to count them one has to introduce an entropy, called configurational entropy or complexity, $s_c = \frac{1}{N} \log \mathcal{N}(f)$, where $\mathcal{N}(f)$ is the number of stationary points with a given free energy density f . The (real space) density profile corresponding to one given minimum is amorphous and lacks any type of periodic long-range order, and different minima are very different from one another. Defining a similarity measure between them, an “overlap” Q (see Eq. (39) below for a precise definition), one typically finds that two minima with the same free energy f have zero overlap. The typical shape of the configurational entropy as a function of f is shown in Fig. 14.

At high temperature, there is typically a single minimum, the high temperature liquid state. There is a temperature below which an exponentially large (in the system size) number of minima appear. Within mean-field models, corresponding to Bethe lattices, completely connected lattices, and interacting particles for $d \rightarrow \infty$ these minima correspond to macroscopic physical states analogous to the periodic minimum corresponding to the crystal. (There is of course no crystal state in disordered systems such as in Eq. (16). In the case

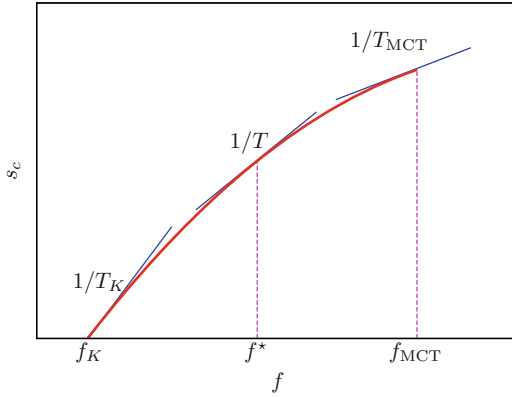
of lattice glass models, there is a crystal phase but it can disappear depending whether the Bethe lattice is a Cayley tree or a random regular graph.) Once the system is in one of these states it remains trapped there forever, since the barriers separating states diverge with the system size. However, when transposed to finite dimensional systems, these states become metastable and have a finite lifetime. As a consequence, in order to compute thermodynamic properties, one has to sum over all of them using the Boltzmann weight $\exp(-\beta N f_\alpha)$ for each state α (Monasson 1995):

$$Z = \sum_{\alpha} e^{-\beta N f_{\alpha}} = \int df \exp[Ns_c(f; T)] e^{-\beta N f}, \quad (21)$$

where $\beta = 1/(K_B T)$. Evaluating this sum by saddle point method yields three regimes. At high temperature, $T > T_{MCT}$, the liquid corresponding to a flat density profile dominates the sum. The landscape is simple and has a single minimum. This is followed by an intermediate temperature regime, $T_K < T < T_{MCT}$, where the sum is dominated by all terms with free energy density satisfying

$$\left. \frac{\partial s_c(f, T)}{\partial f} \right|_{f=f^*} = \beta. \quad (22)$$

There are many of them, the logarithm of their number being given by $Ns_c(f^*, T)$, see Fig. 14 for a graphical solution of Eq. (22). Upon decreasing



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 14 Typical shape of the configurational entropy, s_c , as a function of free energy density, f in the range $T_k < T < T_{MCT}$ for random first-order landscapes. A graphical solution of Eq. (22) is obtained by finding the value of f at which the slope of the curve is $1/T$. Note that s_c is also a function of temperature, so this curve changes with T

the temperature, $s_c(f^*, T)$ decreases until a temperature, T_K , below which the sum in Eq. (21) becomes dominated by only few terms corresponding to states with free energy density f_K given by $s_c(f_K, T) = 0$, see Fig. 14. The entropy in the intermediate temperature range above T_K has two contributions: the one counting the number of minima, given by s_c , and the intra-state entropy, s_{in} , counting the number of configurations inside each state. At T_K , the configurational entropy vanishes, $s_c(T_K) = 0$. As a consequence the specific heat undergoes a jump toward a smaller value across T_K , an exact realization of the “entropy vanishing” mechanism conjectured by Kauzmann (1948).

Let us discuss the dynamical behavior which results from the above analysis. We have already mentioned that relaxation processes do not occur below T_{MCT} because states have an infinite lifetime. The stability of these states can be analyzed by computing the free energy Hessian in the minima (Castellani and Cavagna 2005). One finds that states become more fragile when $T \rightarrow T_{MCT}^-$ are marginally stable at $T = T_{MCT}$, unstable for $T > T_{MCT}$. The relaxation dynamics of these models can be analyzed exactly (Barrat et al. 2004; Maimbourg et al. 2016). Coming from

high temperature, the dynamics slows down and the relaxation time diverges at T_{MCT} in a power law manner,

$$\tau_\alpha \sim \frac{1}{(T - T_{MCT})^\gamma}, \quad (23)$$

where γ is a critical exponent. The physical reason is the incipient stable states that appear close to T_{MCT} . The closer the temperature is to T_{MCT} , the longer it takes to find an unstable direction to relax.

Amazingly, the dynamical transition that appears upon approaching T_{MCT} in random first-order landscapes is completely analogous to the one predicted for supercooled liquids by the Mode-Coupling Theory (MCT) of the glass transition, and developed independently by Leuthesser, Bengtzelius, Götze, Sjolander, and coworkers (Götze 1999). Actually, MCT can be considered as an approximation which becomes controlled and exact for these mean-field models. Originally, MCT was developed using projector operator formalism (Leutheusser 1984; Bengtzelius et al. 1984) and field-theory methods (Das and Mazenko 1986) to yield closed integro-differential equations for the dynamical structure factor in supercooled liquids. These approaches were recently generalized (Biroli and Bouchaud 2004; Biroli et al. 2006) to deal with dynamic heterogeneity and make predictions for the multi-point susceptibilities and correlation functions discussed in section “Dynamic Heterogeneity.” Within MCT, the relaxation timescale diverges in a power law fashion at T_{MCT} , as in Eq. (23). This divergence is accompanied by critical behavior that appears both in space (long range spatial dynamic correlations), and in time (time-dependent power laws).

Comparing Eqs. (1) and (23) makes it clear that MCT cannot be used to describe viscosity data close to T_g since it does not predict activated behavior. It is recognized that an MCT transition at T_{MCT} does not occur in real materials, so that T_{MCT} is, at best, a dynamical crossover. A central advantage of MCT compared to many other theories is that it can yield quantitative predictions from microscopic input obtained for a particular

material. As such it has been applied to scores of different systems, with predictions that can be directly confronted to experimental or numerical measurements. A major drawback is the freedom offered by the “crossover” nature of the MCT transition, so that “negative” results can often be attributed to corrections to asymptotic predictions rather than deficiencies of the theory itself. Nevertheless, MCT has proven to be useful and continues to be developed, applied, and generalized to study many different physical situations (Götze 1999), including aging systems and nonlinear rheology of glassy materials (Berthier et al. 2000; Miyazaki and Reichman 2002; Fuchs and Cates 2002), see also section “Aging and Off-Equilibrium Dynamics.”

What happens below T_{MCT} in a finite dimensional system if the relaxation time does not diverge as predicted in Eq. (23)? Why is the transition avoided? In fact, the plethora of states that one finds in mean-field are expected to become (at best) metastable in finite dimension, with a finite lifetime, even below T_{MCT} . What is their typical life time and how these metastable states are related to the structural relaxation are issues that still await for a complete microscopic analysis.

There exist, however, phenomenological arguments (Xia and Wolynes 2000; Kirkpatrick et al. 1989; Bouchaud and Biroli 2004), backed by microscopic computations (Dzero et al. 2005; Franz 2006) that yield a possible solution dubbed “mosaic state” by Kirkpatrick, Thirumalai, and Wolynes (1989). Schematically, the mosaic picture states that, in the regime $T_K < T < T_{\text{MCT}}$, the liquid is composed of domains of linear size ξ . Inside each domain, the system is in one of the mean-field states. The length of the domains is fixed by a competition between energy and configurational entropy. A state in a finite but large region of linear size l can be selected by appropriate boundary conditions that decrease its free energy by an amount which scales as Yl^θ with $\theta \leq 2$. On the other hand, the system can gain entropy, which scales as $s_c l^3$, if it visits the other numerous states. Entropy obviously gains on large lengthscales, the crossover length ξ being obtained by balancing the two terms,

$$\xi = \left(\frac{Y}{T s_c(T)} \right)^{1/(3-\theta)}. \quad (24)$$

In this scenario, the configurational entropy on scales smaller than ξ is too small to stir the configurations efficiently and win over the dynamically generated pinning field due to the environment, while ergodicity is restored at larger scale. Hence, the relaxation time of the system is the relaxation time, $\tau(\xi)$, of finite size regions. Barriers are finite, unlike in the mean-field treatment. Smaller length scales are faster but unable to decorrelate, whereas larger scales are orders of magnitude slower. Assuming thermal activation over energy barriers which are supposed to grow with size as ξ^ψ , one finally predicts, using Eq. (24), that (Bouchaud and Biroli 2004)

$$\log \left(\frac{\tau_\alpha}{\tau_0} \right) = c \frac{Y}{k_B T} \left(\frac{Y}{T s_c(T)} \right)^{\psi/(3-\theta)}, \quad (25)$$

where c is a constant.

The above argument is rather generic and therefore not very predictive. There exist microscopic computations (Dzero et al. 2005; Franz 2006; Biroli and Cammarota 2017) aimed at putting these phenomenological arguments on a firmer basis and computing the exponents θ and ψ . The results are not yet fully conclusive because they involve replica calculations with some assumptions, but they do confirm the phenomenological scenario presented above and suggest that $\theta = 2$. Some other phenomenological arguments suggest the value of $\theta = 3/2$ (Kirkpatrick et al. 1989). There are no computation available for ψ , only the suggestion that $\psi = 0$ (Kirkpatrick et al. 1989).

Note that using the value $\theta = 3/2$ with $\theta = \psi$ simplifies Eq. (25) into a form that is well-known experimentally and relates $\log \tau_\alpha$ directly to $1/S_c$, which is the celebrated Adam-Gibbs relation (Adam and Gibbs 1965) between relaxation time and configurational entropy that is in rather good quantitative agreement with many experimental results (Angell 1997; Hodge 1997; Johari 2000; Ozawa et al. 2019). The Random First-Order Transition theory can be considered, therefore,

as a microscopic theory that reformulates and generalizes the Adam-Gibbs mechanism. Furthermore, using the fact that the configurational entropy vanishes linearly at T_K , a VFT divergence of the relaxation time as in Eq. (1) is predicted, with the identification that

$$T_0 = T_K. \quad (26)$$

The equality (26) between two temperatures that are commonly used in the description of experimental data certainly constitutes a central achievement of RFOT theory since it accounts for the empirical relation found between the kinetics and the thermodynamics of supercooled liquids. Furthermore RFOT theory naturally contains MCT, which can be used to describe the first decades of the dynamical slowing down, while the spin glass side of RFOT theory qualitatively explains the dynamics in terms of the peculiar features of the free energy landscape that have been detailed above. Dynamics first slows down because there appear incipient metastable states, and once these metastable states are formed, the dynamics becomes dominated by the thermally activated barrier crossing from one metastable state to another, which is consistent with the relation between dynamical correlation length and timescale discussed in section “[Dynamic Heterogeneity](#).” Quite importantly, microscopic computations of T_{MCT} and T_0 for realistic models of liquids are possible (Parisi et al. 2020; Mézard and Parisi 1999).

Probably the most serious weakness of the RFOT theory construction is that the theory, although worked out in full details within mean-field models or the large dimensionality limit, is based for finite dimensions on asymptotic results valid, for example, for $T \rightarrow T_K$. The application of RFOT theory to temperatures accessible in experiments (hence not very close to T_K) requires additional phenomenological assumptions. Moreover, the dynamical processes leading to the VFT law are not understood completely. Although the ultimate consequences of the theory are sometimes in very good agreement with experiments, as Eq. (26), direct tests of the mosaic state picture are rare and difficult (Cavagna et al. 2007; Ozawa and Berthier 2017).

Heterogeneous Disorder and Mapping to the Random, Field Ising Model

The study of second-order phase transitions shows that field theory provides a natural framework to go beyond mean-field theory (Chaikin et al. 1995). With this in mind, researchers in glass physics have also gone down this route in recent years. One of their main achievements has been to identify fluctuations that are neglected by mean-field theory and play a very important role in shaping the physical behavior of supercooled liquids. These fluctuations have been related to the notion of “self-induced disorder” in Franz et al. (2011). In the following, we may prefer the name “self-induced heterogeneity” to make the distinction with the “self-induced disorder” discussed in section “[Franz-Parisi Potential](#).” (This terminology was suggested to us by Jean-Philippe Bouchaud.) The main idea is that when observing equilibrium relaxation from time t to time $t + \tau_\omega$ the state of the system at time t is spatially heterogeneous: for instance it can have higher density in one region and lower density in another. Actually, theoretical analysis shows (Stevenson et al. 2008; Biroli et al. 2018a, b) that even key mean-field quantities, such as the configurational entropy, are heterogeneously distributed in space. Since the amount of slowing down is directly linked to those quantities (at least within RFOT theory), these static fluctuations induce strong dynamical fluctuations, leading in particular to dynamical heterogeneities (Franz et al. 2011). From the theoretical point of view, they play a key role in changing properties of the MCT transition and the ideal glass transition. In fact, even though the MCT transition is like a spinodal instability within mean-field theory (Kirkpatrick and Wolynes 1987b), one finds that once these fluctuations are included, MCT enters the universality class of a disordered spinodal, like, for example, the spinodal of the Random Field-Ising Model (Franz et al. 2011). Using results obtained on this problem, this connection implies that even in the absence of activated hopping, the MCT transition changes nature in any finite dimension: it is either wiped out by non-perturbative fluctuations (Rizzo 2016) or it becomes dominated by rare and non-perturbative

events, as happens for the spinodal of the RFIM (Nandi et al. 2016). One nevertheless expects that the higher the spatial dimension, the more obvious an echo of the MCT mean-field transition should persist (Maimbourg et al. 2016; Biroli and Bouchaud 2012; Berthier et al. 2020).

Finally, the role of heterogeneous disorder on the ideal glass transition has been investigated in Stevenson et al. (2008) and Biroli et al. (2018a, b). The main outcome of these studies is an effective model for the glass transition that takes the form of an RFIM with extra long-range anti-ferromagnetic and multi-body interactions. These new couplings depress the ideal glass transition temperature but do not lead to qualitative changes. The strength of the disorder is, however, crucial: a strong enough disorder (a system-dependent feature) can destroy the ideal glass transition, as may happen for the RFIM. Another relation with the RFIM was also found in Biroli and Bouchaud (2012), where it was shown that amorphous interfaces between rearranging regions behave statistically as the ones of domain walls in the RFIM.

Let us conclude with a word of caution: not everything is understood about self-induced heterogeneity. Since the disorder is strongly linked to the state of the system, it is also to a large extent renewed after a time τ_α , thus it evolves and at the same time it affects the dynamics, that is, it is not truly quenched. This is a first difficulty in assessing precisely its role for glassy relaxation (Berthier et al. 2019c). A second one is that although for static properties, such as configurational entropy or the Franz-Parisi potential, one can establish a mapping to the RFIM, for the dynamics the situation is more intricate and no mapping has been found up to now. (The difficulty is that the mapping to the RFIM proceeds by relating the overlap (for glasses) to the magnetization (for the RFIM). There are no natural dynamical equations for the overlap, and in the only cases where those have been established – the β -regime of MCT – these proved to be quite complex and different from the corresponding equations for the magnetization of the RFIM.)

Renormalization Group for the Glass Transition

In parallel with the efforts described in the previous section, developing a renormalization group (RG) analysis of the glass transition has been a new important theoretical activity in the last decade. Different methods have been used, and were applied on lattice disordered models and replica lattice field theories which display a glass transition. Given that the ideal glass transition has a mixed character, intermediate between first- and second-order phase transition, usual perturbative RG techniques developed for continuous phase transitions do not work. Therefore researchers had to focus on non-perturbative methods. In Castellana et al. (2010) the hierarchical Dyson RG method was employed to analyze the Random Energy Model in finite dimension. The authors found an ideal glass phase transition similar to the one taking place within mean-field but with a nonanalytical behavior of the free-energy at T_K , leading in particular to a specific heat exponent different from one, as assumed within RFOT theory. The real-space properties, correlation length and energy barrier, and the nature of the fixed-point were first studied in Yeo and Moore (2012) and Cammarota et al. (2011) by Migdal-Kadanoff RG. A complete and more advanced analysis was performed in Angelini and Biroli (2017), in which it was shown that the ideal glass transition is associated to a so-called zero temperature fixed point (Fisher 1986). The main implication is that the correlation length and the typical energy barrier have power law divergences with nontrivial exponents, hence implying a super-Arrhenius behavior. However, such a fixed point was found only in dimensions higher than three. In consequence, this RG treatment predicts that in three dimensions the glass transition is actually an avoided phase transition (Kivelson et al. 1995): glassy behavior is still driven by the RG fixed point present in higher dimension, but the correlation length and the timescale do not truly diverge (arguably an irrelevant fact since one cannot approach the transition close enough, but an important conceptual one).

The RG approaches we reviewed above offer a new perspective on the nature of the glass transition. They provide important guidelines for more

controlled non-perturbative RG treatments. Ideally, one would like to tackle directly interacting particle systems in the continuum and use methods that have been proved to be precise and reliable in previous studies, such as the one developed by Wetterich (Berges et al. 2002). This is a formidable challenge as those techniques do not seem to be able to handle the kind of rare and localized non-perturbative events that are relevant for glassy dynamics (Rulquin et al. 2016).

Free Volume, Defects, and Facilitated Models

Lattice Gases

In this subsection we motivate and briefly summarize studies of a different family of statistical mechanics models that turns out to yield a rich variety of physical behaviors. Their starting points are physical assumptions that might seem similar to the models described in section “Random First-Order Transition Theory,” but the outcome yields a different physical explanation of the glass transition. Although the two theoretical approaches cannot be simultaneously correct, they both have been influential and very instructive in order to develop a theoretical understanding of glassy phenomena.

As in section “Random First-Order Transition Theory,” we first consider hard sphere systems. We follow the lattice gas description introduced by Kob and Andersen (1993), and work on a three-dimensional cubic lattice. As in a hard sphere system, we assume no interaction between particles beyond the hard-core constraint that the occupation number n_i at site i is at most equal to 1,

$$H[\{n_i\}] = 0, n_i = 0, 1. \quad (27)$$

In contrast to the lattice glass model, all configurations respecting the hard-core constraint are allowed and are equally probable. Geometric frustration is instead introduced at the level of the kinetic rules, which are defined as constrained local moves. Namely, a particle can jump to a nearest neighbor site only if that site is empty (to satisfy the hard-core constraint), but, additionally, only if the sites occupied before and after the move have less than m neighbors, m being an adjustable parameter, which Kob and Andersen

choose as $m = 4$ for $d = 3$ ($m = 6$ corresponds to the unconstrained lattice gas). The model captures the idea that if the liquid is locally very dense, no movement is possible while regions with low density move more easily.

Of course, such kinetically constrained lattice gases have been studied in various spatial dimensions, for different values of m , for different constraints, or even different lattice geometries (Ritort and Sollich 2003). These models capture the idea of a “cage” effect in a strict sense, meaning that a particle with a dense neighbor shell cannot diffuse. Although the cage seems a purely local concept, it turns out that diffusion in constrained lattice gases arises from cooperative rearrangements, so that slow dynamics can be directly shown to be driven by the growth of dynamic lengthscales for these cooperative moves (Franz et al. 2002; Toninelli et al. 2004; Pan et al. 2005). This strongly suggests that such cooperative moves most probably have a role in the dynamics of real liquids.

Free Volume, Dynamic Criticality

In the lattice gas picture, the connection with the liquid is not obvious because it is the density (“free volume”) rather than the temperature that controls the dynamics. Thermal models with similar features can in fact be defined along the following lines. In a liquid, low temperature implies a very small probability to find a location with enough free volume to move. The idea of a small concentration of “hot spots” is in fact reminiscent of another picture of the glass transition based on the idea of “defects” which is captured by the defect model proposed by Glarum (1960) in the 1960s, where relaxation proceeds via the diffusion of a low concentration of independent defects. In the mid-1980s, using both ideas of kinetic constraints and rare defects, Fredrickson and Andersen defined a family of kinetic Ising models for the glass transition (Fredrickson and Andersen 1984). They studied an assembly of noninteracting spins,

$$H[\{n_i\}] = \sum_{i=1}^N n_i, n_i = 0, 1, \quad (28)$$

where $n_i = 1$ represents the defects, whose concentration becomes exponentially small at low

temperature, $\langle n_i \rangle \approx \exp(-1/T)$. As for the Kob-Andersen lattice gas, the nontrivial ingredient lies in the chosen rates for the kinetic transitions between states. The kinetic rules stipulate that a transition at site i can happen with a usual Glauber rate, but only if site i is surrounded by at least k defects ($k = 0$ corresponds to the unconstrained limit). Again, one can easily imagine studying such models in different spatial dimensions, on different lattices, and with slightly different kinetic rules, yielding a large number of possible behaviors (Ritort and Sollich 2003; Léonard et al. 2007). The similarity between those spin facilitated models and the kinetically constrained lattice gases is striking. Altogether, they form a large family of models generically called kinetically constrained models (KCMs) (Ritort and Sollich 2003).

The connection between KCMs and the much older concept of free volume is obvious from our presentation. Free volume models are among the most widely used models to analyze experimental data, especially in polymeric systems. They have been thoroughly reviewed before (Debenedetti 1996; Cohen and Grest 1982), and the main prediction is that dynamic slowing down occurs because the free volume available to each particle, v_f , vanishes at some temperature T_0 as $v_f \approx \alpha(T - T_0)$. Statistical arguments then relate relaxation timescales to free volume assuming that a movement is possible if locally there is “enough” available free volume, more than a typical value v_0 . This is clearly reminiscent of the above idea of a kinetic constraint for local moves in lattice gases. An appealing VFT divergence is then predicted:

$$\frac{\tau_\alpha}{\tau_0} \sim \exp\left(\gamma \frac{v_0}{v_f}\right) \tilde{\exp}\left(\frac{\gamma v_0/\alpha}{|T - T_0|^\mu}\right), \quad (29)$$

where γ is a numerical factor and $\mu = 1$. Predictions such as Eq. (29) justify the wide use of free volume approaches, despite the many (justified) criticisms that have been raised.

Initially it was suggested that KCMs would similarly display finite temperature or finite density dynamic transitions similar to the one predicted by the mode-coupling theory of supercooled liquids (Fredrickson and Andersen

1984), but it was soon realized (Fredrickson and Brawer 1986; Butler and Harrowell 1991) that most KCMs do not display such singularity, and timescales in fact only diverge in the limit of zero temperature ($T = 0$) or maximal density ($\rho = 1$). Models displaying a $T_c > 0$ or $\rho_c < 1$ transition have also been introduced and analyzed (Toninelli et al. 2006). They provide a microscopic realization, based on well-defined statistical mechanics models, of the glass transition predicted by free volume arguments. Their relaxation timescale diverges with a VFT-like form but with an exponent $\mu \simeq 0.64$. Understanding their universality classes or the degree of generality of the mechanism leading to the transition is still an open problem (Elmatad et al. 2009, 2010; Elmatad and Keys 2012); the most recent results on this front come from mathematical physicists who have been able to classify many of the different possible behaviors on the basis of the microscopic dynamical rules (Hartarsky et al. 2019a, b; Martinelli et al. 2019a, b).

Extensive studies have shown that KCMs have a macroscopic behavior which resembles the phenomenology of supercooled liquids, displaying in particular an Arrhenius or super-Arrhenius increase of relaxation timescales upon decreasing temperature, and non-exponential relaxation functions at equilibrium (Ritort and Sollich 2003). Early studies also demonstrated that, when suddenly quenched to very low temperatures, the subsequent nonequilibrium aging dynamics of these models compares well with experimental observations on the aging of liquids (Fredrickson and Brawer 1986). The diverse definitions of such models suggest a broad variety of different behaviors. This feature is both positive and negative: on the one hand one can explore various scenarios to describe glass transition phenomena, but on the other hand, one would like to be able to decide what particular model should be used to get a quantitative description for a particular liquid. It is not straightforward to perform microscopic predictions using the framework of KCMs, since there is no direct observable parameter to use as input of the theory (unlike $g(r)$, for MCT). An operative definition of KCMs' defects was provided (see next section and Keys et al. (2011,

2013)); however, this does not allow to directly choose which KCM (which rules) are appropriate for a given liquid.

Despite this caveat, it is quite useful to use KCMs as theoretical tools to define concepts and obtain new ideas. It is precisely in this perspective that interest in KCMs has increased, in large part since it was realized that their dynamics is spatially heterogeneous (Franz et al. 2002; Butler and Harrowell 1991; Garrahan and Chandler 2002), a central feature of supercooled liquids dynamics. In particular, virtually all the aspects related to dynamic heterogeneity mentioned in section “Dynamic Heterogeneity” can be investigated and rationalized, at least qualitatively, in terms of KCMs. The dynamics of these systems can be understood by considering where “relaxation” happens and then propagate, which is dictated by the underlying defect motion (Ritort and Sollich 2003). Depending on the particular model, defects can diffuse or have a more complicated motion. Furthermore, they can be point-like or “cooperative” (formed by point-like defects moving in a cooperative way). A site can relax only when it is visited by a defect. As a consequence, the heterogeneous character of the dynamics is entirely encoded in the defect configuration and defect motion (Garrahan and Chandler 2002). For instance, a snapshot similar to Fig. 6 in a KCM shows clusters which have relaxed within the time interval t (Whitelam et al. 2005; Berthier and Garrahan 2005). These are formed by all sites visited by a defect between 0 and t . The other sites are instead frozen in their initial state. In these models the dynamics slows down because the defect concentration decreases. As a consequence, in the regime of slow dynamics there are few defects and strong dynamic heterogeneity. Detailed numerical and analytical studies have indeed shown that in these systems, non-exponential relaxation patterns do stem from a spatial, heterogeneous distribution of timescales, directly connected to a distribution of dynamic lengthscales (Toninelli et al. 2004, 2006; Pan et al. 2005; Garrahan and Chandler 2002; Whitelam et al. 2005; Jack et al. 2006a). Decoupling phenomena also appear naturally in KCMs and can be shown to be very direct,

quantifiable, consequences of the dynamic heterogeneity (Jung et al. 2004), which also deeply affects the process of self-diffusion in a system close to its glass transition (Berthier et al. 2004). More fundamentally, multipoint susceptibilities and multipoint spatial correlation functions such as the ones defined in Eqs. (8) and (11) can be studied in much greater detail than in molecular systems, relating their evolution to time and length scales (Berthier et al. 2007b; Toninelli et al. 2005; Pan et al. 2005; Chandler et al. 2006; Whitelam et al. 2004). This type of scaling behavior has been observed close to $T = 0$ and $\rho = 1$ in spin models and lattice gases without a transition. (Acritical (diérent) behavior is expected and predicted for models having a transition (Toninelli et al. 2006).) Different theoretical approaches have shown that these particular points of the phase diagram correspond to genuine critical points where timescales and dynamic lengthscales diverge with well-defined critical laws (Jack et al. 2006a; Whitelam et al. 2004). Such “dynamic criticality” implies the existence of universal scaling behavior in the physics of supercooled liquids, of the type reported for instance in Fig. 11.

Defects: Connection with Hamiltonian Dynamics Models

A central criticism about the free volume approach, that is equally relevant for KCMs, concerns the identification, at the molecular level, of the vacancies (in lattice gases), mobility defects (in spin facilitated models), or of the free volume itself. The attempts to provide reasonable coarse-graining from molecular models with continuous degrees of freedom to lattice models with kinetic rules have been, for a very long time, quite limited and not fully convincing (Gebremichael et al. 2004; Downton and Kennett 2007).

For molecular models, this issue was first attacked in 2010, with a definition of the cumulated dynamical activity K , an extensive quantity characterizing the frequency of state changes (from excited to non-excited and vice versa) (Elmatad et al. 2010; Hedges et al. 2009). This definition was made more concrete and studied in models of supercooled liquids in Keys et al. (2011), where an appropriate functional is

explicitly designed as a recorder of excitations (or defects). Defects or excitations are not to be mistaken with displacements. Indeed, some locations providing opportunities for structural reorganization do coincide with defects, and their presence can be inferred by observing nontrivial particle displacements associated with transitions between relatively long-lived configurations. Displacements instead refer to dynamical moves in short segments of a trajectory, while defects refer to underlying configurations. The explicit definition of defects has since been used to estimate the role of facilitation in glassy dynamics, to provide a microscopic validation of KCMs (Keys et al. 2015; Isobe et al. 2016), to explain dynamical heterogeneities in glassy materials, or to compute the dynamical facilitation volume (Elmatad and Keys 2012).

The conceptual proof that kinetic rules emerge effectively and induce a slow dynamics has been obtained for simple lattice spin models (Garrahan 2002), with a dynamics that directly maps onto constrained models. A deeper study of this kind of model was performed more recently (Turner et al. 2015). Several examples are available but here we only mention the simple case of the bidimensional plaquette model defined by a Hamiltonian of a p-spin type on a square lattice of linear size L ,

$$H = -J \sum_{i=1}^{L-1} \sum_{j=1}^{L-1} S_{i,j} S_{i+1,j} S_{i,j+1} S_{i+1,j+1}, \quad (30)$$

where $S_{i,j} = \pm 1$ is an Ising variable lying at node (i, j) of the lattice. Contrary to KCMs, the Hamiltonian in Eq. (30) contains genuine interactions, which are no less (or no more) physical than p-spin models discussed in section “Random First-Order Transition Theory.” Interestingly the dynamics of this system is (trivially) mapped onto that of a KCM by analyzing its behavior in terms of plaquette variables, $p_{i,j} = S_{i,j} S_{i+1,j} S_{i,j+1} S_{i+1,j+1}$, such that the Hamiltonian becomes a non-interacting one, $H = -J \sum_{i,j} p_{i,j}$, as in Eq. (28). More interestingly, the analogy also applies to the dynamics (Garrahan 2002). The fundamental moves are spin-flips, but when a single spin is flipped the states of the four plaquettes

surrounding that spin change. Considering the different types of moves, one quickly realizes that excited plaquettes, $p_{i,j} = +1$, act as sources of mobility, since the energetic barriers to spin flips are smaller in those regions. This observation allows to identify the excited plaquettes as defects, by analogy with KCMs. Spatially heterogeneous dynamics, diverging lengthscales accompanying diverging timescales and scaling behavior sufficiently close to $T = 0$ can be established by further analysis (Jack et al. 2005), providing a simple but concrete example of how an interacting many body system might effectively behave as a model with kinetic constraints. (This type of plaquette models and other spin models were introduced originally (Lipowski et al. 2000; Sethna et al. 1991) to show how ultraslow glassy dynamics can emerge because of growing free energy barriers.)

Connection with Other Perspectives

An essential drawback of facilitated models is that among the microscopic “details” thrown away to arrive at simple statmech models such as the ones in Eqs. (27) and (28), information on the thermodynamical behavior of the liquids has totally disappeared. In particular, a possible coincidence between VFT and Kauzmann temperatures, T_0 and T_K is not expected, nor can the dynamics be deeply connected to thermodynamics, as in Adam-Gibbs relations. The thermodynamical behavior of KCMs appears different from the one of real glass-formers close to T_g (Biroli et al. 2005). This is probably the point where KCMs and RFOT approaches differ most obviously. Even though the dynamics of KCMs shares similarities with systems characterized with a complex energy landscape (Berthier and Garrahan 2003; Whitelam and Garrahan 2004), thermodynamical behaviors are widely different in both cases, as has been recently highlighted in Jack and Garrahan (2005) by focusing on the concrete examples of plaquette models such as in Eq. (30).

Finally, when KCMs were first defined, they were argued to display a dynamical transition of a very similar nature to the one predicted by MCT (Fredrickson and Andersen 1984). Although the claim has been proven wrong, it bears some truth:

both approaches basically focus on the kinetic aspects of the glass transition and they both predict the existence of some dynamic criticality with diverging lengthscales and timescales. (Most KCMs do not have a finite temperature dynamical transition and the ones displaying a transition have critical properties different from MCT.) This similarity is even deeper, since a modecoupling singularity is present when (some) KCMs are studied on the Bethe lattice (Toninelli et al. 2004), but is “avoided” when more realistic lattice geometries are considered (Berthier et al. 2012).

Geometric Frustration, Avoided Criticality, and Locally Preferred Structures

In all of the above models, “real space” was present in the sense that special attention was paid to different lengthscales characterizing the physics of the models that were discussed. However, apart from the “packing models” with hard-core interactions, no or very little attention was paid to the geometric structure of local arrangements in molecular liquids close to a glass transition. This slight oversight is generally justified using concepts such as “universality” or “simplicity,” meaning that one studies complex phenomena using simple models, a typically statistical mechanics perspective. However, important questions remain: what is the liquid structure within mosaic states? How do different states differ? What is the geometric origin of the defects invoked in KCMs? Are they similar to defects found in crystalline materials (disclinations, dislocations, vacancies, etc.)? Some lines of research attempt to provide answers to these questions, making heavy use of the concept of geometric frustration.

Geometric Frustration

Broadly speaking, frustration refers to the impossibility of simultaneously minimizing all the interaction terms in the energy function of a system. Frustration might arise from quenched disorder (as in the spin glass models described above), but liquids have no quenched randomness. In liquids, instead, frustration has a purely geometrical origin. It is attributed to a competition between a short-range tendency for the extension of a

“locally preferred order,” and global constraints that prevent the periodic tiling of space with this local structure.

This can be illustrated by considering once more the packing problem of spheres in three dimensions. In that case, locally the preferred cluster of spheres is an icosahedron. However, the fivefold rotational symmetry characteristic of icosahedral order is not compatible with translational symmetry, and formation of a periodic icosahedral crystal is impossible (Frank 1952). The geometric frustration that affects spheres in three dimensional Euclidean space can be relieved in curved space (Nelson 2002). In Euclidian space, the system possesses topological defects (disclination lines), as the result of forcing the ideal icosahedral ordering into a “flat” space. Nelson and coworkers developed a solid theoretical framework based on this picture to suggest that the slowing down of supercooled liquids is due to the slow wandering of these topological defects (Nelson 2002), but their treatment remains too abstract to obtain quantitative, explicit results. Further theoretical work extended the integral-equation approach to calculate the pair correlation function in hyperbolic geometry, making it easier to compare predictions and simulation data (Sausset et al. 2009). MCT was also re-derived in curved space (on a sphere), showing that it still cannot capture quantitatively the transition (Vest et al. 2014, 2015). Explicit numerical results were also obtained recently (Turci et al. 2017a), showing a clear first-order like transition from liquid to ordered solid in an appropriately curved space, becoming avoided as Euclidean space is retrieved.

Coulomb Frustrated Theories

The picture of sphere packing disrupted by frustration has been further developed in simple statistical models characterized by geometric frustration, in a pure statistical mechanics approach (Tarjus et al. 2005). To build such a model, one must be able to identify, then capture, the physics of geometric frustration. Considering a locally ordered domain of linear size L , Kivelson et al. (1995) suggest that the corresponding free energy scales as

$$F(L, T) = \sigma(T)L^2 = \phi(T)L^3 + s(T)L^5. \quad (31)$$

The first two terms express the tendency of growing locally preferred order and represent respectively the energy cost of having an interface between two phases and a bulk free energy gain inside the domain. Geometric frustration is encoded in the third term which represents the strain free energy resulting from frustration. The remarkable feature of Eq. (31) is the super-extensive scaling of the energy cost due to frustration which opposes the growth of local order. The elements in Eq. (31) can then be directly incorporated into ferromagnetic models where “magnetization” represents the local order, ferromagnetic interactions represent the tendency to local ordering, and Coulombic antiferromagnetic interactions represent the opposite effect, coming from the frustration. The following Hamiltonian possesses these minimal ingredients:

$$H = -J \sum_{\langle i, j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + K \sum_{i \neq j} \frac{\mathbf{S}_i \cdot \mathbf{S}_j}{|\mathbf{x}_i - \mathbf{x}_j|}, \quad (32)$$

where the spin $\mathbf{S}_i$ occupies the site i at position $\mathbf{x}_i$. Such Coulomb frustrated models have been studied in great detail, using various approximations to study models for various space and spin dimensions (Tarjus et al. 2005).

The general picture is that the ferromagnetic transition occurring at $T = T_c^0$ in the pure model with no frustration ($K = 0$) is either severely displaced to lower temperatures for $K > 0$, sometimes with a genuine discontinuity at $K \rightarrow 0$, yielding the concept of “avoided criticality.” For the simple case of Ising spins in $d = 3$, the situation is different since the second-order transition becomes first-order between a paramagnetic phase and a spatially modulated phase (stripes). For $K > 0$ and $T < T_c^0$ the system is described as a “mosaic” of domains corresponding to some local order, the size of which increases (but does not diverge!) when T decreases. Tarjus, Kivelson, and coworkers clearly demonstrated that such a structuration into mesoscopic domains allows one to understand most of the fundamental phenomena occurring in supercooled liquids (Tarjus et al.

2005). Their picture as a whole is very appealing because it directly addresses the physics in terms of the “real space,” and the presence of domains of course connects to ideas such as cooperativity, dynamic heterogeneity, and spatial fluctuations, which directly explains, at least qualitatively, non-exponential relaxation, decoupling phenomena, or super-Arrhenius increase of the viscosity. However, as for the RFOT mosaic picture, direct confirmations of this scenario are rare (Coslovich and Pastore 2007), or difficult to obtain.

Locally Preferred Structures

Going back to the geometric structure of local arrangements in real space, a line of research has emerged that is based upon some kind of local order (Coslovich 2011; Royall and Williams 2015; Malins et al. 2013a, b). Icosahedral order was initially shown to be linked to the dynamics of some binary mixtures. But more generally, for simple enough glass-formers, a broader variety of locally ordered structures can be defined (Royall and Williams 2015), such as, for example, defective icosahedron (Royall and Kob 2017). A vast body of literature has shown that these locally preferred structures (LPS) seem to correlate with structural relaxation. Using trajectory path sampling (see section “*s-Ensemble and Large Deviations*”), it was found that LPS and dynamic activity play equivalent roles, and are therefore strongly correlated (Turci et al. 2017b, 2018). The increased number of LPS has also been linked to hindered crystallization (Turci et al. 2019). These multiple effects suggest the LPS impacts the dynamics in various ways.

For several systems in $d = 2, 3$, simple local order parameters measuring the distance from sterically favored structures (sixfold symmetry, angles, and closeness to local tetrahedron) have been spatially coarse-grained (Tong and Tanaka 2018), thus revealing a clear structure-dynamics relationship. The interpretation in Tong and Tanaka (2018) is that these LPS represent an indirect measurement of the true amorphous order. The very simple and widespread tetrahedral order has been observed in a variety of materials (Shi and Tanaka 2019). The LPS-dynamics correlation has also been confirmed recently in experiments on colloids (Hallett et al. 2018; Pinchaipat

et al. 2017), providing further evidence of the important role of LPS in glassy behavior.

Despite these important advances, the concrete application of LPS-based techniques on any particular realistic glass-forming material is hindered by the lack of a universal operative definition of the LPS. For relatively simple systems, an operative scheme was designed to automatically find these LPS (Royall and Williams 2015; Mossa and Tarjus 2006).

A natural alternative to this tedious exercise is the use of modern machine learning techniques. In particular, one may consider the unsupervised learning task of grouping together similar local structures (this is called clustering). Once clusters (corresponding to automatically found LPS) are found, any local environment may be assigned to its most similar group (LPS), but without the burden of defining the LPS's one by one (Ronhovde et al. 2011, 2012; Paret et al. 2020; Boattini et al. 2020).

Mean-Field Theory of the Amorphous Phase

The phase transition between liquid and glass is not the only interesting phenomenon characterizing the phase diagram of glassy materials. Since the transition occurs at finite pressure and temperature, glasses can be further compressed or cooled within the glass phase itself (Kurchan et al. 2012, 2013; Biroli and Urbani 2018; Rainone and Urbani 2016; Rainone et al. 2015; Scalliet et al. 2019a). How do physical properties of glasses change in this context? In mean-field theory, this question has been widely investigated by using the hard spheres glass model (Parisi and Slanina 2000; Parisi and Zamponi 2010), a favorite canonical example of a glass-former system because of its analytical simplicity. Eventually, by compressing a hard sphere glass, the system undergoes the jamming transition in the limit of infinite pressure (Donev et al. 2004). In this section, we briefly survey recent progress in the development of an analytic theory of the glass phase in the large d limit, with a particular emphasis on hard spheres (Parisi et al. 2020).

Mean-Field Glassy Phase Diagrams

When a glass-forming liquid undergoes the glass transition, it becomes confined into a single free energy minimum and the timescale to explore different minima becomes infinite. It is formally possible to define thermodynamic properties by restricting the available statistical configurations to a single free energy minimum. This can be enforced in the replica formalism by considering two copies of the system and constraining the distance between them (Charbonneau et al. 2017). First, an equilibrium reference configuration $\underline{Y}$ at $(T_g, \hat{\varphi}_g)$ is introduced, where $\hat{\varphi}$ is the scaled packing fraction $\hat{\varphi} = 2^d \varphi / d$. Second, a copy of the equilibrium configuration $\underline{X}(t)$ is created and evolved in time. Let us define now the mean-squared displacement (MSD) between the two copies as $\langle \Delta(\underline{X}, \underline{Y}) \rangle = \Delta_r$. The properties of $\underline{X}(t)$ are sampled in a restricted region of phase space close to the equilibrium configuration. Within this state following construction, the system at $(T_g, \hat{\varphi}_g)$ with initial configuration $\underline{Y}$ can be adiabatically followed anywhere in the glass phase diagram.

Concretely, for the glass state selected by $\underline{Y}$ and followed until $(T, \hat{\varphi})$, we can write the restricted partition function as:

$$Z[T, \hat{\varphi} | \underline{Y}, \Delta_r] = \int d\underline{X} e^{-\beta V(\underline{X})} \delta(\Delta_r - \Delta(\underline{X}, \underline{Y})), \quad (33)$$

where $V(\underline{X})$ is the potential energy of the configuration $\underline{X}$, and the delta function enforces the restricted average. In order to obtain the glass free energy, we need to compute its average over the chosen reference configuration $\underline{Y}$, which acts as a source of quenched disorder:

$$f_g(T, \hat{\varphi} | T_g, \hat{\varphi}_g, \Delta_r) = -\frac{T}{N} \int \frac{d\underline{Y}}{Z[T_g, \hat{\varphi}_g]} e^{-\beta_g V(\underline{Y})} \times \ln Z[T, \hat{\varphi} | \underline{Y}, \Delta_r] \quad (34)$$

where $Z[T_g, \hat{\varphi}_g] = \int d\underline{Y} \exp^{-\beta_g V(\underline{Y})}$ is the partition function at $(T_g, \hat{\varphi}_g)$. Mathematically, the

quenched disorder is handled using the replica method. We then introduce $(n + 1)$ replicas of the original system, with the initial glass at $(T_g, \hat{\varphi}_g)$ being the master replica, while the n other slave replicas describe the glass at $(T, \hat{\varphi})$. The glass free energy is finally expressed in terms of the average MSD between the slave replicas and the master replica Δ_s , and the average distance between the slave replicas Δ . At this step, we assume that the symmetry between slave replicas is not broken, which corresponds to the 1RSB ansatz described in section “Random First-Order Transition Theory.”

By choosing the state point at $(T, \hat{\varphi}) = (T_g, \hat{\varphi}_g)$, the recursive equations for Δ and Δ_s have to satisfy $1/\hat{\varphi} = \mathcal{F}_\beta(\Delta)$, where $\mathcal{F}_\beta(\Delta)$ is a positive function which vanishes for both $\Delta \rightarrow \infty$ and $\Delta \rightarrow 0$, with an absolute maximum in between. This equation can then be satisfied only if

$$\frac{1}{\hat{\varphi}_d} \leq \max_{\Delta} \mathcal{F}_\beta(\Delta). \quad (35)$$

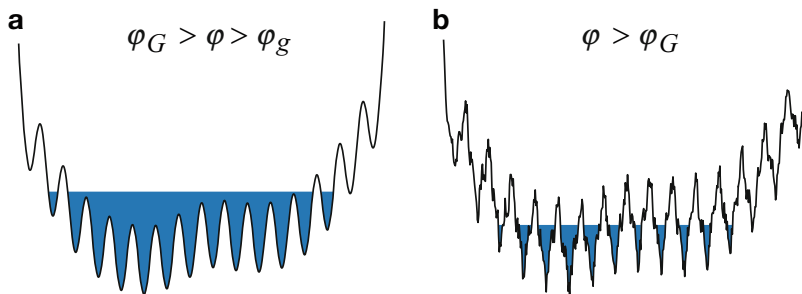
This condition occurs for volume fractions larger than a critical value $\hat{\varphi}_d(\beta_g)$, which corresponds to the dynamical glass transition.

We can explore the glass phase following the glass prepared at the glass transition $(T_g, \hat{\varphi}_g)$ at different temperatures and packing fractions. At low T and high $\hat{\varphi}$ one eventually meets another phase transition (Kurchan et al. 2013), where the

1RSB assumption fails (Mézard et al. 1987) and the more complex full-replica symmetry breaking (fullRSB) solution is necessary to compute the glass free energy, the so-called Gardner phase transition (Gardner 1985; Berthier et al. 2019d). Here, the fullRSB solution corresponds to a hierarchical organization of the distances between the slave replicas and the glass becomes marginally stable (Rainone and Urbani 2016; Franz et al. 2017). The emergence of a complex free energy landscape gives rise to nontrivial dynamical processes (Scalliet and Berthier 2019; Liao and Berthier 2019; Scalliet et al. 2019b). A pictorial representation of the Gardner transition is shown in Fig. 15.

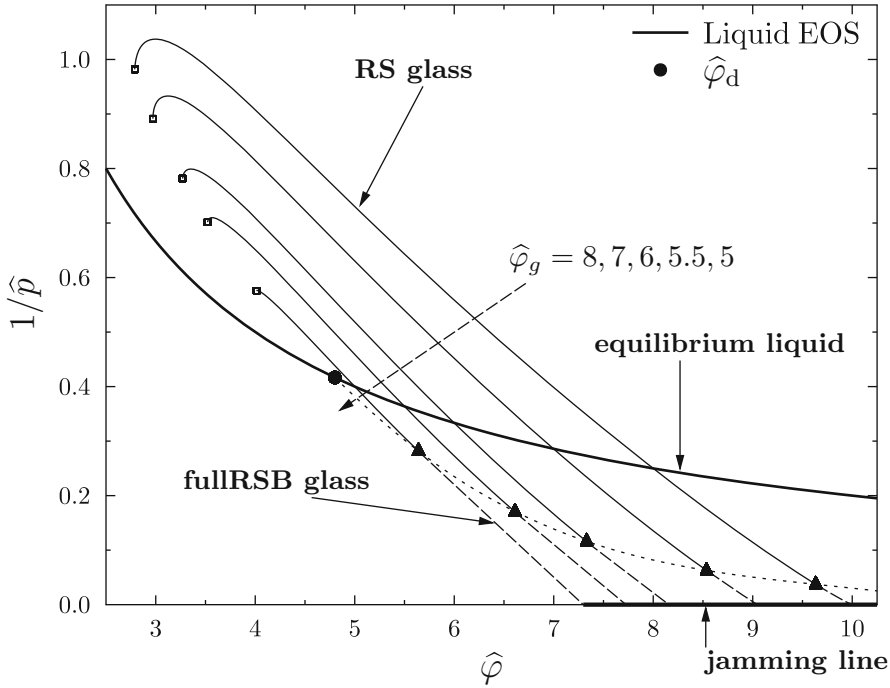
It is worth noting that the derivation sketched above is completely general and can be used for any glassy pair potential mentioned in section “Random First-Order Transition Theory.” In the following we will apply this formalism to the hard spheres model, for which several implications from the mean field picture have been successfully tested numerically (Charbonneau et al. 2014b; Berthier et al. 2016a). Here, the relevant state parameter is the scaled reduced pressure $\hat{p} = \beta P / \rho d$. We refer to Biroli and Urbani (2016, 2018), Berthier et al. (2019d), and Scalliet et al. (2017, 2019a, b) for more results regarding systems made of soft potentials.

Starting from an equilibrated hard sphere liquid configuration at $\hat{\varphi}_g$, we can apply the state following formalism to explore the hard sphere phase diagram in Fig. 16. The reduced pressure can be computed from the equation of state of an infinite dimensional hard sphere liquid $\hat{p}\hat{\varphi}/2$,



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 15 (a) Sketch of the free energy structure deep in the hard sphere glass phase, where each basin

breaks down in sub-basins corresponding to secondary relaxations. At the Gardner transition in (b), the sub-basins become fractal and ergodicity is broken



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 16 Phase diagram of hard spheres in the inverse reduced pressure – reduced peaking fraction ($1/\hat{p}, \hat{\phi}$) plane. The glass transition is marked by a full circle. The glass equations of state are reported as full lines in the region where the replica symmetric solution is stable.

The Gardner transition is marked by triangles, beyond which the fullRSB solution is stable (dashed lines). Tice glass equations of state end at the jamming transition. Upon decompression, glasses are stable until a spinodal instability arises (open squares)

derived from a Virial expansion of the free energy (Maimbourg et al. 2016). Starting from $\hat{\phi}_g$ and decompressing the system, the glass eventually undergoes a melting transition: the 1RSB solution becomes unstable and the glass melts into the liquid via a spinodal instability (Kurchan et al. 2013). Upon compression instead, the glass enters deeper into the glass phase and remains dynamically arrested. Numerically, this has been proven by measuring Δ as the long-time limit of the MSD $\Delta(t)$ between the system at time t and the initial configuration at $t = 0$. The order parameter of the transition Δ_r is instead computed as the long-time limit of the distance $\Delta ab(t)$ between two copies A and B of the same initial system evolved with different initial velocities:

$$\Delta_{AB} = \left\langle \frac{1}{N} \sum_{i=1}^N |\mathbf{r}_i^A - \mathbf{r}_i^B|^2 \right\rangle. \quad (36)$$

Upon further compression, the glass eventually undergoes the Gardner transition at a finite pressure $\hat{p}_G$. Here, the relation between Δ_r and Δ breaks down and $\Delta(t)$ is characterized by a logarithmic growth in time, suggesting the emergence of a complex free energy landscape (Berthier et al. 2016a). The copies A and B cannot occupy the same sub-basin and are no longer able to explore the entire metabasin. Due to the fractal nature of the free energy landscape, the excitations required to move around the fractal states correspond to soft modes (Scalliet et al. 2019b). The correlation length of these modes can be estimated by measuring the dynamical susceptibility, computed as the variance of Δ_{AB} , which indeed shows a divergence at the Gardner transition (Berthier et al. 2016a).

Compressing further within the Gardner phase, the pressure eventually diverges as the system reaches its jamming density $\hat{\phi}_J$, which depends

explicitly on the selected initial condition $(T_g, \hat{\varphi}_g)$. In particular, there exists a range of jamming points, or a “jamming line” (Chaudhuri et al. 2010), whose extension increases with d (Kurchan et al. 2012).

Jamming

During the last two decades, a large research effort has shed light on the critical behavior characterizing the jamming transition (Liu and Nagel 2010). Jamming can be seen from two different perspectives. An assembly of Brownian hard spheres under compression becomes rigid at a finite density, at which point the pressure diverges. On the other hand, athermal packings of soft repulsive spheres reach the jamming point under decompression when the pressure vanishes. In both situations, each particle is constrained by enduring contacts with the neighbor particles and the system is rigid. In particular, at jamming the average number of contacts per particle Z reaches the critical value $Z_c = 2d$, which represents the lower limit for mechanical stability (O’Hern et al. 2002) (Maxwell’s criterion for rigidity). From the hard spheres side, Z jumps from zero to Z_c at the transition, while from the soft spheres side, as the pressure decreases toward zero the excess number of contacts scales as (Ohern et al. 2003; Durian 1995):

$$\Delta Z = Z - Z_c \tilde{\Delta\varphi}^{1/2}, \quad (37)$$

where $\Delta\varphi = \varphi - \varphi_J$ is the amount of compression above the jamming threshold. A connection between hard and soft spheres at jamming is observed in the pair correlation function (Donev et al. 2005; Ohern et al. 2003), confirming that allowed configurations of hard and soft spheres are identical at jamming.

When $\Delta Z = 0$ the system is isostatic, that is, there are just enough contacts to ensure mechanical stability and the system is marginally stable: breaking a bond between contacts can lead to an excitation that causes a collective motion throughout the whole system (Wyart 2012). Not surprisingly, this critical behavior fits well into the free energy picture of marginal glasses reported above.

Marginality in athermal jammed solids can be explained in real space by the so-called cutting argument (Wyart et al. 2005). Imagine removing the contacts between a subsystem of linear size l and the rest of the system. If we slightly compress the system, this cutting will lead to a competition between the overall excess contacts ΔZ created by the compression, and the missing contacts at the boundary of the subsystem. If the total number of contacts is below the isostatic value $N_{iso} = NZ/2$, then there are modes with no energetic cost, that is, soft modes. The number of soft modes N_{soft} then corresponds to the difference between the number of contacts at the boundary, proportional to l^{d-1} , and the number of extra contacts created by the compression, which scales as $\Delta Z l^d$. There is then a critical length $l^* \sim \Delta\varphi^{-1/2}$ for which the system looks isostatic and for $l = l^*$, soft modes correlate over the whole subsystem. These extended anomalous modes correspond to random excitations over all the system, profoundly different from acoustic modes proper of crystalline solids.

Other anomalies of jammed solids are observed in the scaling of the elastic moduli near the transition. These critical behaviors have been successfully described within a force network picture, for which an effective medium theory has been developed (Wyart 2010; Degiuli et al. 2015). In particular, a jammed soft sphere configuration can be mapped onto a network of springs with elastic contacts k_{eff} , computed as second derivatives of the pairwise interaction between particles. The resulting scaling behaviors for the bulk modulus $B \sim k_{eff}$ and the shear modulus $G \sim k_{eff} \Delta\varphi^{1/2}$ suggest that the Poisson ratio $G/B \sim \Delta\varphi^{1/2}$ vanishes at the jamming transition (Ohern et al. 2003). This criticality reflects on the frequency of normal modes which is directly related to the elastic moduli ($B(\omega)$, $G(\omega)$) by the dispersion relation $\omega^* = ck^*$, where $k^* \sim 1/l^*$ and c is the speed of sound. Since sound propagates either longitudinally (B) or transversely (G), two different length scales can be defined: the longitudinal length scale $l^* \sim \Delta\varphi^{-1/2}$, which matches the cutting length scaling behavior and is indeed attributed to extended soft modes, and the transverse length scale which follows the scaling $l_t \sim \Delta\varphi^{-1/4}$.

Other critical scaling laws have been predicted both by replica mean field calculations and effective medium theory for a spring network, with good consistency with numerical results in finite dimensions. In particular, the distributions of interparticle voids and interparticle forces follow universal power laws (Charbonneau et al. 2012, 2015; DeGiuli et al. 2014; Lerner et al. 2013). Contact forces can be either extended or localized, with distributions defined by power law exponents θ_e and θ_l , respectively. Extended forces are predicted from the infinite dimensional exact solution, whereas the localized forces likely result from the presence of localized defects, such as rattling particles, which only exist in finite dimensions. Remarkably, the numerical value of the critical exponents associated to scaling laws near jamming can be predicted analytically in the mean-field approach (Charbonneau et al. 2014a, b; Parisi et al. 2020), and their value is confirmed by numerical simulations in dimensions $d \geq 2$.

The influence of temperature on the jamming criticality has also been studied (DeGiuli et al. 2015; Ikeda et al. 2013). These works show that above jamming there exists a region in the plane $T - \varphi$ where the harmonic approximation of the soft sphere potential holds, and the vibrational spectrum converges to its zero temperature limit, provided that $T < T^*(\varphi)$. The value of $T^*(\varphi)$ decreases with $\Delta\varphi \rightarrow 0$ with a trivial scaling exponent. A similar result holds below jamming for hard sphere glasses (Brito and Wyart 2009). For $T > T^*(\varphi)$, the harmonic approximation breaks down, defining an anharmonic critical regime, controlled by nonanalyticities in the interparticle potential. Physically, strong anharmonicities stem from the constant breaking and reformation of particle contacts in the presence of thermal fluctuations (Schreck et al. 2011).

Vibrational Properties

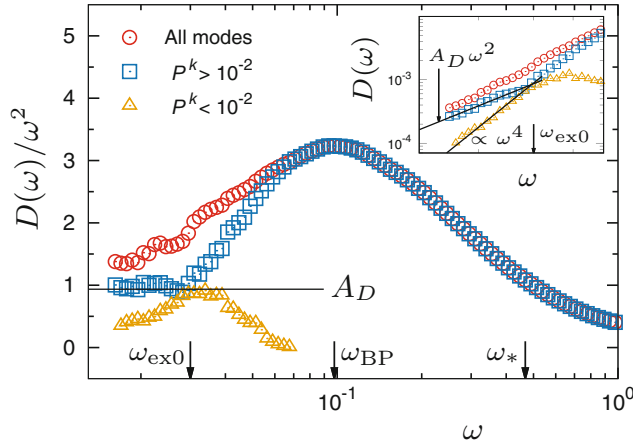
The anomalous thermal properties of low temperature glasses can be related to the structure of the free energy landscape of glassy states. Amorphous solids behave very differently from crystalline solids. In terms of heat capacity and thermal conductivity, crystals are dominated by phononic

excitations with a low-frequency density of states (DOS) $D(\omega)$ given by the Debye scaling law $D(\omega) \sim \omega^{d-1}$. Instead, the thermal properties of glasses are dominated by an excess of vibrational modes referred to as the boson peak and by an anomalous low-frequency scaling of $D(\omega)$. This excess of anomalous vibrations reflects, within mean-field theory, the existence of multiple free energy barriers in glassy states. In fact, when the glass enters the Gardner phase, the system becomes marginal and even infinitesimal perturbations lead to excitations that can bring the system to a different glassy state.

The mean-field theory of glasses has been explored using soft spheres in the jamming limit (Franz et al. 2015). The theory predicts the low-frequency scaling of the vibrational density of states (vDOS) to be $D(\omega) \sim \omega^2$ in any dimension (Parisi and Zamponi 2010; Wyart 2010; Berthier et al. 2011b), quite differently from the Debye scaling. The same result was previously obtained within the effective medium theory (DeGiuli et al. 2014).

Numerically, the nature of the low-frequency vibrational spectrum has been widely studied using soft spheres packings close to jamming. Early studies suggested the existence of the $D(\omega) \sim \omega^2$ scaling (Charbonneau et al. 2014b; Franz et al. 2015) for a wide range of dimensions d , reinforcing the relevance of the mean-field description for finite dimensional systems (Charbonneau et al. 2016a). The modes giving rise to this scaling form have been found to be extended anomalous modes. A more recent study established that the ω^2 scaling is only observed over a finite frequency range, which seems to increase systematically with the space dimension d , which is consistent with a pure quadratic scaling when $d = \infty$. However, for any finite d , the density of states eventually obeys Debye scaling for sufficiently low frequencies.

Finally, recent numerical works show that for frequencies lower than the boson peak, an additional family of soft modes due to marginal instabilities can be observed (Mizuno et al. 2017; Lerner et al. 2016). As Fig. 17 shows, the vibrational density of these additional modes scales as ω^4 .



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 17 Adapted from (Mizuno et al. 2017). Vibrational density of states of jammed harmonic soft spheres scaled by the Debye law ω^{d-1} in $d = 3$. Modes with index k are classified as extended (blue) or localized

(yellow) by their participation ratio P^k . Below the boson peak frequency ω_{BP} , the density of states is the superposition of anomalous extended modes eventually obeying Debye scaling, and a population of quasi-localized modes scaling as ω^4 , as confirmed in the inset

A spatial analysis of such modes shows that they correspond to quasi-localized modes, which are again absent from the large d analytic description.

Rheology

Once the glass is created, it can be adiabatically cooled or compressed, but it can also be deformed by applying an external mechanical constraint. The rheology of amorphous solids is a very broad research field. Here, we present recent results in this field obtained using the mean field glass theory, including implications regarding elasticity, yielding, and shear jamming (Rainone and Urbani 2016; Rainone et al. 2015; Biroli and Urbani 2016; Yoshino and Zamponi 2014).

We report results obtained from the same state following formalism applied to study the amorphous phase along a compression in the $d \rightarrow \infty$ limit. If the master replica $\underline{Y}$ is in the dynamically arrested region, the system reacts elastically to a small applied strain γ . We can then obtain the stress-strain curve as a function of the state point $(T, \hat{\varphi})$ of the slave replica $\underline{X}$. The stress for an elastic medium increases linearly with strain, which defines the shear modulus $\hat{\mu} = \frac{d\hat{\sigma}}{d\gamma}$ computed at zero strain, where stress and shear modulus are scaled such that the $d \rightarrow \infty$ limit remains finite. In the small strain limit one finds

$$\hat{\mu} = \frac{1}{\Delta} \quad (38)$$

where Δ is the long time limit of the MSD. The MSD $\Delta(\underline{X}, \underline{Y})$ is the superposition of an affine component due to the strain, and of a non-affine contribution defined by the particular shear protocol. At the glass transition, the shear modulus jumps from a zero value (liquid state) to a finite value at $\hat{\varphi}_d$ (glass state). In finite dimensions, this sharp discontinuity becomes a crossover (Parisi et al. 2020).

When the system is confined within a glass state, it is able to sustain a shear strain on a time scale which corresponds to the diverging time scale for which the dynamics becomes diffusive. One can then follow adiabatically the slave replica until a state point $(T, \hat{\varphi})$ and study the linear response to shear for the different phases of the glass. This corresponds to exploring the strain vs volume fraction phase diagram of the system. Upon decompression, the shear modulus decreases and displays a square root singularity at the melting spinodal point (Parisi et al. 2020; Rainone et al. 2015).

Increasing the strain and/or the volume fraction, the glass phase may undergo a Gardner transition and transform into a marginal glass, for which all nonlinear elastic moduli diverge and

standard elasticity theory does not hold anymore (Biroli and Urbani 2016). As for a simple compression without shear, the boundary of the Gardner phase transition explicitly depends on the selected glass state.

Once the Gardner phase is entered, upon further compression or strain, two kinds of transition may occur in hard sphere glasses. First, the shear modulus may increase and eventually diverge when a jamming point is reached. At zero strain, this is the ordinary jamming transition. In that case, the power law scaling of the MSD directly implies a similar behavior for the shear modulus. In the presence of a finite strain, this corresponds to the phenomenon of shear jamming, observed in the context of granular materials (Urbani and Zamponi 2017; Peters et al. 2016).

A second type of instability can occur when increasing the strain of a hard sphere glass. Here, the shear stress reaches a maximum followed by a spinodal instability where the fullRSB solution for Δ and Δ_r is no longer stable. The spinodal point $\gamma_Y(\hat{\varphi}_g)$ corresponds to the glass yielding transition (Urbani and Zamponi 2017; Parisi et al. 2017). The yielding transition in glasses has been studied for a variety of models and under different physical conditions (Lin et al. 2014; Ozawa et al. 2018b). In particular, it has been suggested that the yielding transition belongs to the same universality class as the RFIM, that is, a spinodal transition with disorder.

New Computational Methods

In the last decade, a number of new numerical techniques have allowed to attack the challenges presented in the above theoretical sections. These techniques typically make use of tools that go beyond the realm of standard computer simulations to either sample phase space more efficiently or access information and observables that are not directly stored in particle trajectories.

The Swap Monte-Carlo Method

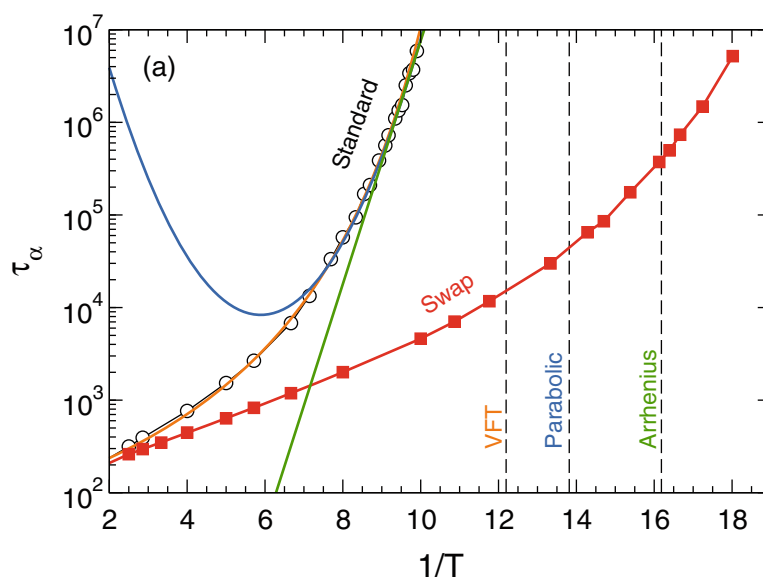
To sample deeply supercooled states in equilibrium, one needs to run computer simulations over

a duration that scales with the equilibrium structural relaxation time τ_α . Because τ_α grows rapidly as the system approaches the glass transition, ordinary computer simulations are limited to a rather high temperature regime much above the experimental glass transition T_g .

The swap Monte Carlo algorithm is an efficient way to produce equilibrium configurations of a supercooled liquid on the computer (Berthier et al. 2016b; Ninarello et al. 2017). Here, “efficient” means that the equilibration time of the swap Monte Carlo algorithm increases much less than τ_α as temperature decreases. Actually, it was shown that for several three-dimensional model systems, the equilibration speedup can be larger than a factor 10^{11} , as illustrated in Fig. 18. For this particular model of soft spheres, the swap algorithm continues to reach thermal equilibrium below the experimental glass transition T_g .

The swap algorithm was introduced long ago (Gazzillo and Pastore 1989), and it was first used in the context of the glass transition by Grigera and Parisi (2001). Its ability to reach equilibrium at extremely low temperatures was established more recently (Berthier et al. 2016b; Ninarello et al. 2017; Ninarello 2017). By comparison with ordinary computer simulations, the swap Monte Carlo algorithm introduces unphysical particle moves, where the identity of a pair of randomly chosen particles is exchanged. Provided the swap moves are constructed to satisfy detailed balance, the algorithm is guaranteed to reach thermal equilibrium. The swap Monte Carlo algorithm can be implemented in a molecular dynamics setting, replacing the swap moves by an exchange between the system and a reservoir of particles (Brito et al. 2018; Kapteijns et al. 2019; Berthier et al. 2019e). Typically, increasing the frequency of swap moves speeds up the dynamics but there are practical limits to the maximal allowed frequency (Berthier et al. 2019e). The swap algorithm was shown to work well from $d = 2$ up to at least $d = 8$ dimensions (Berthier et al. 2019f).

A decisive step to increase the efficiency of the swap Monte Carlo algorithm was the development of models for supercooled liquids that were tailored to increase the swap efficiency. However, and perhaps more importantly, many models that



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 18 From (Ninarello et al. 2017). Relaxation times for standard (open symbols) and swap (closed symbols) Monte Carlo dynamics. The standard dynamics is fitted with the VFT, parabolic, and Arrhenius laws, which

are then used to estimate the location of the experimental glass temperature T_g (vertical dashed lines). The swap dynamics efficiently equilibrates the system at temperatures below T_g

were previously thought to be good glass-formers were in fact crystallizing very easily when swap was employed. Thus, a key step was also the development of more robust glass-forming models, using size polydispersity and nonadditive interaction parameters to prevent structural ordering (Ninarello et al. 2017; Parmar et al. 2020).

In summary, the swap Monte Carlo algorithm easily and rapidly produces a large number of independent equilibrium configurations of a glass-former over a very broad range of temperatures, from the high temperature liquid, down to the mode-coupling crossover, and even below the experimental glass transition temperature. The latter regime can be explored experimentally only using physical vapor deposition, see section “[Ultrastable Glasses](#).” Therefore, many physical properties of glassy materials can now be measured over a temperature regime that is extremely broad, and may be compared directly to experiments with no extrapolation. This has led to an important activity to address several problems related to glassy materials: the Gardner transition in finite dimensional glass-formers (Liao and

Berthier 2019; Scalliet et al. 2019b; Berthier et al. 2016a), the link between glass and jamming transitions (Berthier et al. 2016b; Coslovich et al. 2018), the measurement of the configurational entropy in deeply supercooled liquids (Ozawa et al. 2018c; Berthier et al. 2019g), the analysis of point-to-set lengthscales (Berthier et al. 2017c; Yaida et al. 2016) and of the Franz-Parisi potential (Berthier et al. 2017c; Guiselin et al. 2020), the evolution of several important properties of glasses with the glass preparation (Khomenko et al. 2020; Wang et al. 2019a; Wang et al. 2019b), and the physics of ultrastable glasses (Berthier et al. 2017b; Flenner et al. 2019).

In addition, the demonstration that a very simple algorithm can speed up the equilibration dynamics of supercooled liquids can be seen as an interesting physical result in itself. If such a result appears quite natural in the context of kinetic facilitation (Wyart and Cates 2017; Gutiérrez et al. 2019), it is more challenging (but possible) to interpret in the context of the random first-order transition theory (Berthier et al. 2019c; Ikeda et al. 2017b; Szamel 2018),

where dynamics becomes highly collective at very low temperatures.

Franz-Parisi Potential

In seminal work (Franz and Parisi 1997; Franz and Parisi 1998), Franz and Parisi introduced a quantity now called the Franz-Parisi potential, $V(Q)$. This quantity plays the role of a Landau free energy for mean-field phase transitions, in the sense that it expresses the free energy cost of the order parameter fluctuations at the mean-field level.

For spin glass models, where the approach was first introduced, the overlap Q represents indeed the spin glass order parameter. It quantifies the degree of similarity between two configurations C_0 and C_1 . For liquids with continuous degrees of freedom, a practical definition of the overlap reads:

$$Q = \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N \Theta\left(a - |\mathbf{r}_i^{C_0} - \mathbf{r}_j^{C_1}|\right), \quad (39)$$

where $\mathbf{r}_i^{C_0}$ represents the position of particle i in configuration C_0 . The overlap is close to unity when the two configurations C_0 and C_1 have similar density profiles, up to thermal vibrations of spatial extension a (typically, one takes a as a small fraction of the particle diameter, $a \sim 0.2\sigma$).

The Franz-Parisi potential $V(Q)$ efficiently captures all the features associated to a random first-order transition. It can be defined from the probability distribution function $P(Q)$ of the overlap as $V(Q) = - (T/N) \log P(Q)$. In particular, $V(Q)$ is characterized by a single minimum near $Q = 0$ at high temperature, but develops within mean-field theory a secondary minimum at a finite $Q > 0$ when T decreases toward the Kauzmann transition, indicating that the glass phase is metastable with respect to the liquid. The free energy difference between the glass and the liquid phases in this regime is given by $TS_c(T)$, where $S_c(T)$ is the configurational entropy. Physically, this means that localizing the system in a single free energy minimum in the liquid phase comes with a free energy cost of entropic nature.

In addition, Franz and Parisi introduced a field ε conjugate to the overlap Q :

$$H_{FP}[C_1] = H[C_1] - \varepsilon Q[C_0, C_1]. \quad (40)$$

This allowed them to explore an extended phase diagram by changing both T and ε (Cardenas et al. 1999; Donati et al. 2002). In this plane, the Kauzmann transition at $(T = T_K, \varepsilon = 0)$ extends as a first-order transition line, which ends at a second-order critical point at a position $(T_c > T_K, \varepsilon_c)$. More recent work taking into account finite dimensional fluctuations suggest that this critical point should exist also in finite dimensions, and should be in the same universality class of the random field Ising model (Biroli et al. 2014).

The Franz-Parisi potential and the extended phase diagram have been studied numerically in finite dimensional models in recent years (Turner et al. 2015; Berthier et al. 2017c; Guiselin et al. 2020; Cardenas et al. 1999; Berthier 2013; Biroli et al. 2016; Berthier and Jack 2015; Jack and Garrahan 2016; Parisi and Seoane 2014). Taken together, these studies confirm the existence of both a first-order transition line and a second-order RFIM critical point in finite dimensional glass-formers.

A second important outcome of the Franz-Parisi potential is the possibility to directly estimate a configurational entropy for equilibrium glass-formers using the free energy difference between the liquid and metastable glass phase (Berthier et al. 2017c; Berthier and Coslovich 2014). This definition of the configurational entropy is conceptually closer to its mean-field definition, and does not rely on an explicit definition of metastable states for a finite dimensional system (Berthier et al. 2019a).

Point-to-Set Lengthscale

As mentioned in section “Static and Dynamic Correlation Functions,” assessing and measuring a growing static length scale is crucial to the glass problem. Standard probes used for second-order phase transitions, such as 2-point and 4-point correlation functions, do not seem to provide any useful evidence. A possible explanation is that

these correlation functions do not carry enough information to capture the relevant structural order, also termed amorphous order, and that one has to use higher-order correlation functions (see also section “[Jamming Transition](#)”). The point-to-set correlation function $C(R)$ is effectively an n -point correlation function, where n is the number of particles comprised in a sphere of radius R (the “set”), which can indeed be a large number.

The justification is that in order to probe amorphous order one has to proceed as in standard phase transitions: fix a suitable boundary condition and study whether it enforces a given arrangement of particles in the bulk of the system. For simple cases, such as the ferromagnetic Ising model, it is clear what type of boundary conditions are needed (all spins up or all spins down). However, for supercooled liquids this is a much harder task. The problem can be circumvented by using equilibrated configurations and freezing all particles outside a cavity of radius R . This provides the boundary conditions sought for: if the system is indeed ordering, then using cavities drawn from different equilibrium configurations will give access to different sets of appropriate boundary conditions. This method was first proposed theoretically in the context of RFOT theory (Bouchaud and Biroli 2004; Montanari and Semerjian 2006) and signal processing (Mézard and Montanari 2006), and was transformed into a concrete numerical procedure in Cavagna et al. (2007) and Biroli et al. (2008). In the last decades, measurements of the point-to-set length were progressively refined (Berthier and Kob 2012; Berthier et al. 2016c, 2017c; Yaida et al. 2016; Cavagna et al. 2012; Charbonneau et al. 2016b).

Let us describe the main steps and mention some important obstacles that had to be overcome. Firstly, one needs a collection of well-equilibrated configurations C_0 to start with. This is not supposed to be the hardest part, but for very low temperatures, methods such as the swap Monte Carlo algorithm are necessary.

Secondly, for each sample C_0 one freezes all particles outside a cavity of radius R , then let the particles inside ergodically visit the remaining phase space, and record the configurations C_1 that are sampled. For small cavities, large

activation barriers make conventional molecular dynamics simulations ineffective, but this problem can be solved using parallel tempering techniques (Berthier et al. 2016c), in addition to swap Monte Carlo (Cavagna et al. 2012). It is crucial to check that a complete sampling of the restricted configurational space has been reached inside the cavity, and careful tests have been devised to this end (Cavagna et al. 2012).

Thirdly, one needs to measure the overlap distribution $P(Q)$ between the quenched reference configuration C_0 and the equilibrium samples C_1 . This is very similar to the Franz-Parisi construction, except for the local nature of the constraint. There are two possibilities. One is that the cavity is so small that only one state (one configuration, up to vibrations) can be visited, so that the peak of $P(Q)$ is in the high-overlap range. The other is that the cavity is sufficiently large for many different states to be accessible. In that case, $P(Q)$ has a peak at low Q . In between the two cases, there is a critical value of the radius, $R \sim \xi_{PTS}$, which corresponds to the crossover, with a bimodal $P(Q)$. Since finite size cavities cannot be self-averaging, one needs to repeat the overlap measurements for many independent quenched configurations C_0 , and then perform an average over these realizations of the disorder. Indeed, for $R \sim \xi_{PTS}$, large sample-to-sample variations of $P(Q)$ are observed.

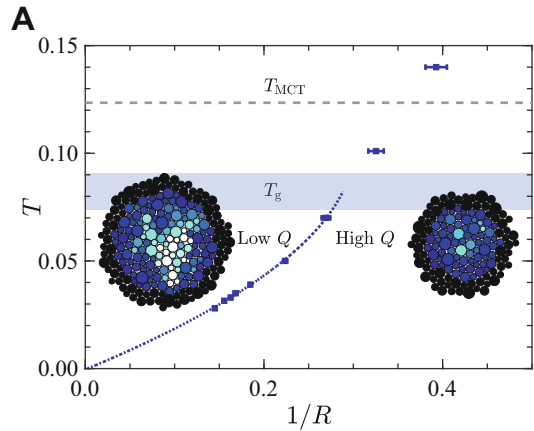
There are a number of subtleties and extensions related to the overlap function that we now describe. A first subtlety is that an appropriate measure of the overlap needs to focus on the center of the spherical cavity, since boundaries always have a high overlap, and this makes the results difficult to interpret (Biroli et al. 2008). Moreover, the overlap needs to be a smooth function of the distance between configurations, and step functions are too singular to average over. A second subtlety is that for some liquids, the simple positional information does not adequately cover all the structural information. In that case, the conventional overlap needs to be completed with additional coordinates overlap, for example, bond angles. This was used in Yaida et al. (2016) to show that hexatic order could be captured by the point-to-set correlations (see also Russo and Tanaka 2015).

Let us also mention a few extensions of the method that have been proposed. In Cavagna et al. (2012), the authors proposed to relax the frozen configuration constraint by letting the outside atoms vibrate, so long as they maintain a large overlap with the initial configuration: they called this reference state “frozen state” (as opposed to frozen configuration). A second type of extension is to study various confinement geometries, as in Berthier and Kob (2012), Kob et al. (2012), Cavagna et al. (2012), and Li et al. (2014), where it was shown that the geometry of confinement needs to be carefully considered.

Thanks to the computational progress outlined above, several important results were established in the last decade. Among them: (i) clear evidence that the slowing down of the dynamics is accompanied by the growth of the point-to-set length (even though a mild one), (ii) established relation between point-to-set and configurational entropy: the former appears to be inversely proportional to the other (Berthier et al. 2019a), thus directly linking the growth of amorphous order to the decrease in number of metastable states – a tenet of RFOT theory, (iii) clear difference between two-dimensional and three-dimensional behavior: two-dimensional glass-formers display a point-to-set that appears to diverges at zero temperature, as shown in Fig. 19, thus indicating a $T_K = 0$ Kauzmann transition temperature (Berthier et al. 2019g). This is in sharp contrast with the results in three dimensions, where the extrapolated T_K is larger than zero.

s-Ensemble and Large Deviations

The Franz-Parisi potential is an example of a large deviation analysis. The idea behind it is that fluctuations in the overlap field play an important role for the glass transition, analog to the magnetization field in a ferromagnet. In order to investigate such fluctuations, one can then study the large deviation function (the free-energy) associated to the spatial average of the field (the order parameter). This is the usual route followed in thermodynamic analyses of second-order phase transitions. The s-ensemble is the dynamical counterpart of such a procedure. One modifies the dynamical rules, in order to be in a particular subset of the “dynamical states,” to probe the tendency of the



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 19 From Berthier et al. (2019g). Evolution of the inverse point to set length, denoted here as $1/R$ with the temperature T . A clear growth of the point to set length up to $\xi_{PTS} \approx 6.5$ is observed. Cavities smaller (larger) than ξ_{PTS} have a large (small) overlap with the reference configuration, as illustrated in the snapshots, where the particle shade encodes the overlap value

original system to explore these states. This idea originates both from theoretical considerations on the large deviations of activity (rare events) predicted in KCMs (Garrahan et al. 2007, 2009) and from considerations on efficient simulation schemes (for rare events as well) that apply more generally (Noe et al. 2009). In practice, the s-ensemble dynamics is a particular instance of transition path sampling, where the quantity of interest is a measure of the activity of a multi-particles trajectory $\{x_i(t)\}_{i=1, \dots, N}$, cumulated over time

$$K[x(t)] = \frac{1}{N t_{obs}} \sum_{t \in [t_0, t_0 + t_{obs}]} \sum_{i \in [1, N]} (x_i(t + \Delta t) - x_i(t))^2 \quad (41)$$

where Δt (resp. t_{obs}) is chosen to be of the order of a few ballistic times (resp. a few relaxation times). In the s-ensemble, the actual relaxation time then becomes larger than t_{obs} . Here we follow the notations used in (Hedges et al. 2009), where this biasing method was first applied to structural glasses (for its initial introduction in KCMs, see Elmatad et al. (2010), and Garrahan et al. (2007, 2009)). The method is called s-ensemble because the probability

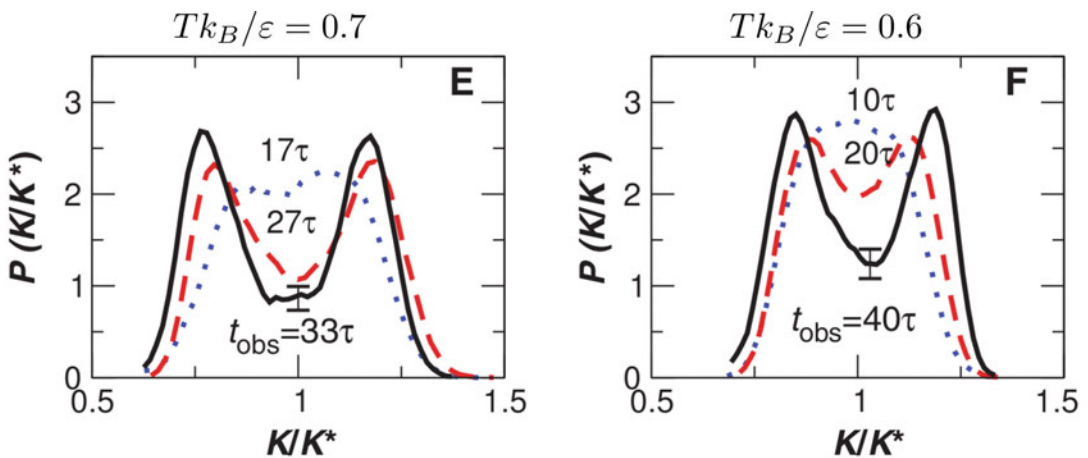
of a trajectory $x(t)$ is $P_0[x(t)]e^{-sK[x(t)]}$, where $P_0[x(t)]$ is the probability for the unperturbed system. This amounts to defining a “thermodynamics of trajectories” which are biased (and classified) depending on their activity; s is the biasing field. In order to numerically simulate and probe such a measure, one can perform Monte-Carlo sampling in trajectory space. This method is actually so efficient at finding low-energy states that special attention must be paid to crystallization (Hedges et al. 2009).

One of the most important results obtained by the s -ensemble method is a direct evidence of a first-order phase transition between an active phase (for low s) and an inactive phase (for large s) in supercooled liquids: see Fig. 20. In the $s - T$ plane this corresponds to a first-order transition line $s^*(T)$ which ends in a critical point at high temperature (Elmatad et al. 2010; Hedges et al. 2009). Although the method focuses on the dynamical properties, inactive states do exhibit interesting structural features. They are more stable than equilibrium samples (Jack et al. 2011): mechanically, in terms of their lower number of low-energy modes (depletion of $D(\omega)$), and thermodynamically, in terms of a longer lived “melting” transient from the glass to the liquid state. This suggests that inactive states correspond to very stable glassy state, that is, nonequilibrium glassy states with low fictive temperatures.

The foundation of the s -ensemble relies on the dynamical behavior of KCMs. For the East model scenario it was shown (Keys et al. 2015) that configurations obtained by (i) the s -ensemble, (ii) finite-rate cooling, and (iii) quenching and longtime aging are all equivalent. This provides a concrete example where glassiness is directly related to the phase transition unveiled by the s -ensemble. Let us conclude by noticing that even systems having an RFOT display such a phase transition, the difference being that the line $s^*(T)$ reaches $s^* = 0$ for $T = T_K$ and not for $T = 0$ as for KCMs (Jack and Garrahan 2010). This shows that the s -ensemble is actually a general construction, which transforms the physics of metastability observed in supercooled liquids in well-defined phase transitions in the extended ensemble comprising space and time.

Machine Learning Developments

We have mentioned the possible use of (unsupervised) Machine Learning (ML) in section “Geometric Frustration, Avoided Criticality, and Locally Preferred Structures” for automatic identification of LPS in supercooled liquids (see also Ronhovde et al. 2011, 2012; Paret et al. 2020; and Boattini et al. 2020). Another set of ML techniques to be used is supervised learning: automatically defining fluid- or solid-like structures (features in



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 20 From Hedges et al. (2009). Coexistence of the active (large K) and inactive (small K) phases, as evidenced from s -ensemble biased simulations. As

temperature is reduced, the distribution becomes increasingly bimodal, as expected when approaching a first-order phase transition

ML language) by labeling them for a training set of local environments which are observed to be locally fluid-or solid-like. The general idea developed in Schoenholz (2018) is to train a neural network (or other fitting model) to “predict” the current degree of mobility or “instantaneous activity” from the knowledge of structure only. This may be cast as finding the function f such that $f\left(\left\{\vec{r}\right\}\right) \times (i, t) = y_{\text{prel}} \approx y_{\text{true}}(i, t)$, where $\left\{\vec{r}\right\}(i, t)$ is the structure of the neighborhood of particle i at time t , and $y_{\text{true}}(i, t)$ (the label) is a measure of the dynamical activity for particle i at time t . Concretely, the target label y_{true} has to encode some notion of local, instantaneous mobility (Candelier et al. 2009, 2010a, b), while the local structure may be defined, for example, by the (local, instantaneous) density pair correlation function $\mathbf{g}(\mathbf{r})$, with the possible addition of angular variables (Cubuk et al. 2016; Schoenholz et al. 2016). This technique has been applied with success, showing how much structure correlates with dynamics in supercooled liquids (Schoenholz et al. 2016; Landes et al. 2020), disordered solids (Cubuk et al. 2016; Schoenholz et al. 2015, 2016; Landes et al. 2020; Cubuk et al. 2015), for the plasticity of amorphous materials (Ivancic et al. 2017; Cubuk et al. 2017), and in polycrystalline materials (Sharp et al. 2018).

The problem of the interpretation, which is one of the major issues with statistical learning in general, remains open: how to make use of predictions emerging from hundred-parameters models? This issue is transverse to most ML applications and is currently under active scrutiny. In terms of basic science, the conclusion of Liu and collaborators is that the predicted y_{pred} provides a new observable, called the softness field (Schoenholz et al. 2015), which plays a key role for the dynamics.

We conclude mentioning a very recent work which introduced a new ML technique in the glass physics arena. The authors of (Bapst et al. 2020) focused on the problem of predicting long-time dynamics (more precisely, the propensity field (Widmer-Cooper and Harrowell 2006)) from knowledge of structure alone, by leveraging on recent progress in graph neural networks. The results are impressive: the ability to predict the

propensity map is substantially better than existing numerical physics-based methods and the ML techniques described above, thus establishing a promising new way to study glassy dynamics.

Aging and Off-Equilibrium Dynamics

Why Aging?

We have dedicated most of the above discussion to properties of materials approaching the glass transition at thermal equilibrium. We discussed a rich phenomenology and serious challenges for both our numerical and analytical capabilities to account for these phenomena. For most people, however, glasses are interesting below the glass transition, so deep in the glass phase that the material seems to be frozen forever in a seemingly arrested amorphous state, endowed with enough mechanical stability for a glass to retain, say, the liquid it contains (preferably a nice red wine). Does this mean that there is no interesting physics in the glass state?

The answer is clearly “no.” There is still life (and physics) below the glass transition. We recall that for molecular glasses, T_g is defined as the temperature below which relaxation is too slow to occur within an experimental timescale. Much below T_g , therefore, the equilibrium relaxation timescale is so astronomically large that thermal equilibrium is out of reach. One enters therefore the realm of off-equilibrium dynamics. A full physical understanding of the nonequilibrium glassy state remains a central challenge (Young 1998; Barrat et al. 2004).

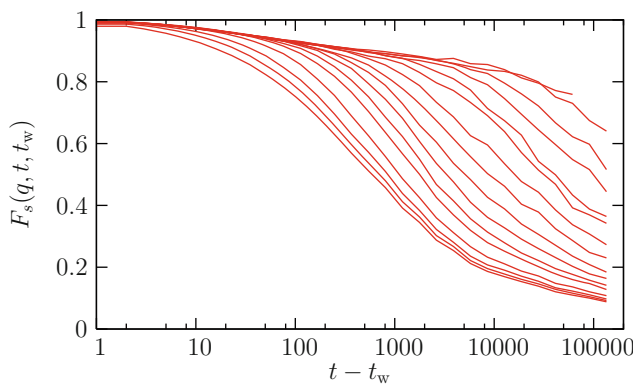
A first consequence of studying materials in a time window smaller than equilibrium relaxation timescales is that the system can, in principle, remember its complete history, a most unwanted experimental situation since all details of the experimental protocol may then matter. The simplest protocol to study aging phenomena in the glass phase is quite brutal (Struik 1977): take a system equilibrated above the glass transition and suddenly quench it at a low temperature at a “waiting time” $t_w = 0$ which corresponds to the beginning of the experiment. For $t_w > 0$ the

system is left unperturbed at constant temperature where it tries to slowly reach thermal equilibrium, even though it has no hope to ever get there. Aging means that the system never forgets the time t_w spent in the glass phase, its “age.” The evolution of one time quantities, for example, the energy, as a function of time is not a good evidence of aging. In order to show that the system never equilibrates, two time quantities such as density-density or spin-spin correlation functions are much more useful. A typical example is presented in Fig. 21 where the self-part of the intermediate function in Eq. (5) is shown for a Lennard-Jones molecular liquid at low temperature. Immediately after the quench, the system exhibits a relatively fast relaxation: particles still move substantially. However, when the age increases, dynamics slow down and relaxation becomes much slower. When t_w becomes very large, relaxation becomes too slow to be followed in the considered time window and the system seems frozen on that particular timescale: it has become a glass. A striking feature conveyed by these data is that an aging system not only remains out-of-equilibrium for all practical purposes, but its typical relaxation time is in fact set by its age t_w . In simple cases, the effective relaxation time after waiting a time t_w scales at t_w itself, which means that since equilibration timescales have diverged,

t_w is the only remaining relevant timescale in the problem.

A popular interpretation of this phenomenon is given by considering trap models (Bouchaud 1992). In this picture, reminiscent of the Goldstein view of the glass transition mentioned above (Goldstein 1969), the system is described as a single particle evolving in a complex energy landscape with a broad distribution of trap depths – a paradigmatic mean-field approach. Aging in this perspective arises because the system visits traps that become deeper when t_w increases, corresponding to more and more stable states. It therefore takes more and more time for the system to escape, and the dynamics slow down with time, as observed in Fig. 21. This implies that any physical property of the glass becomes an age-dependent quantity in aging protocols, and more generally becomes dependent on how the glass was prepared. One can easily imagine using this property to tune mechanical or optical characteristics of a material by simply changing the way it is prepared, like how fast it is cooled to the glassy state (recall our discussion of ultrastable glasses in section “Ultrastable Glasses”).

A real space alternative picture was promoted in particular in the context of spin glass studies, based on the ideas of scaling and renormalization (Bray and Moore 1984; van Hemmen and



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 21 Aging dynamics in a Lennard-Jones glass-forming liquid at low temperature. The system is quenched at time $t_w = 0$ at low T , where the temperature is kept constant. Two-time self-intermediate scattering

functions are then measured for 20 logarithmically spaced waiting times t_w from $t_w = 1$ to $t_w = 10^5$ (from left to right). The relaxation becomes slower when t_w increases: the system ages

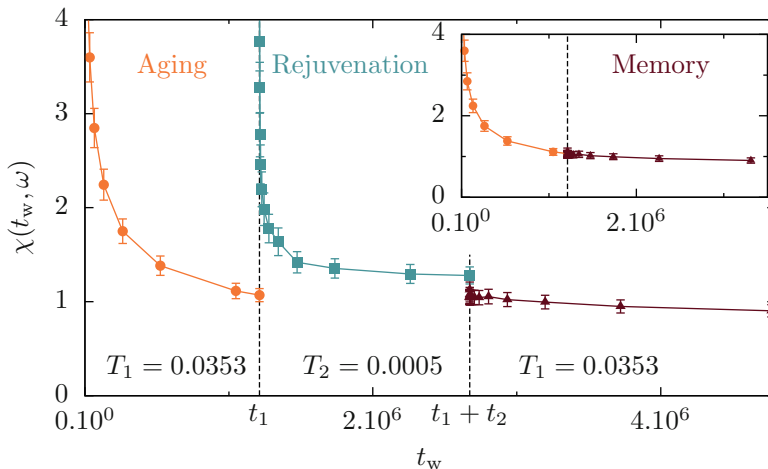
Morgenstern 1987; Fisher and Huse 1986). The physical picture is that of a coarsening process, where the system develops long-range order by growing extended domains of lengthscale $\ell(t_w)$. On lengthscales less than $\ell(t_w)$, the system has had the time to order since the quench at $t_w = 0$. The walls between domains evolve in a random environment. In order to move they have to overcome free energy barriers. It is then assumed an activated dynamic scaling which states that the typical barrier to extend the domain from linear size $\ell(t_w)$ to, say, $2\ell(t_w)$ scales as ℓ^ψ , where ψ is some “barrier” exponent. Using the Arrhenius law to relate dynamics to barriers, one gets that aging corresponds to the logarithmic growth with time of spatially correlated domains, $\ell \sim (T \log t_w)^{1/\psi}$. A domain growth picture of aging in spin glasses can be directly confirmed by numerical simulations (Kisker et al. 1996), only indirectly by experiments.

Memory and Rejuvenation Effects

Since the complete history of a sample in the glass phase matters, there is no reason to restrain experimental protocols to the simple aging experiment mentioned above. Indeed, experimentalists have

investigated scores of more elaborated protocols that have revealed an incredibly rich, and sometimes quite unexpected, physics (Young 1998). We restrain ourselves here to a short discussion of memory and rejuvenation effects observed during temperature cycling experiments (Refregier et al. 1987) (one can imagine applying a magnetic field or a mechanical constraint, be they constant in time or sinusoidal, etc.). These two effects were first observed in spin glasses, but the protocol was then repeated in many different materials, from polymers and organic liquids to disordered ferroelectrics. After several unsuccessful attempts, similar effects are now observed in numerical work as well (Berthier and Young 2005; Berthier and Bouchaud 2002). Recent results obtained from simulations of a three-dimensional glass-former exploring the spin-glass-like Gardner phase (Scalliet and Berthier 2019) are presented in Fig. 22.

There are three steps in temperature cycling experiments (Refregier et al. 1987). The first one is a standard aging experiment, namely a sudden quench from high to low temperature at time $t_w = 0$. The system then ages for a duration t_1 at constant temperature T_1 . The system slowly



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 22 Memory and rejuvenation effects obtained in the numerical simulation of a three-dimensional glass-former (Scalliet and Berthier 2019). There is a first aging step, $0 < t_w < t_1$, during which the system slowly tries to reach thermal equilibrium at

temperature T_1 . The system “rejuvenates” in the second step at T_2 , $t_1 < t < t_1 + t_2$, and it restart aging (rejuvenation). Finally in the third step, temperature is back to T_1 , and memory of the first step is kept intact, as shown in the inset where relaxation during the second step of the experiment is taken away

relaxes toward equilibrium and its dynamics slows down: for our spin glass example (see Fig. 22) this is observed through the measurement of some dynamic susceptibility $\chi(t_w, \omega)$. Temperature is then suddenly shifted to $T_2 < T_1$ at time t_1 . There, the material restarts aging (almost) as if the first step had not taken place. This is called “rejuvenation effect,” because the system seems to forget it is already “old.” At total time $t_1 + t_2$, temperature is then shifted back to its initial value T_1 . Then, aging is found to proceed as a quasi-perfect continuation of the first step, as if the second step had not taken place. The system has kept the “memory” of the first part of the experiment, despite the rejuvenation observed in the intermediate part. The memory effect becomes more spectacular when relaxation during the second step is removed, as in the inset of Fig. 22. The third relaxation appears indeed as a perfect continuation of the first one.

On top of being elegant and quite intriguing, such protocols are relevant because they probe more deeply the dynamics of aging materials, allowing one to ask more precise questions beyond the simplistic observation that “this material displays aging.” Moreover, the observation of similar effects in many different glassy materials implies that these effects are intrinsic to systems with slow dynamics. Interesting also are the subtle differences observed from one material to the other.

Several experimental, numerical and theoretical papers have been devoted to this type of experiments, and these effects are not “mysterious” anymore (see Barrat et al. (2004)). A clear link between memory effects and typical lengthscales over which the slow dynamics takes place has been established. Because lengthscales depend so sensitively on timescales and on the working temperature, experiments performed at two different temperatures typically probe very different lengthscales, allowing the system to store memory of its state at different temperatures over different lengthscales (Berthier and Bouchaud 2002; Bouchaud et al. 2001). In return, this link has been elegantly exploited to obtain a rather precise experimental estimate of dynamic lengthscales involved in the aging dynamics of spin glass materials (Bert et al. 2004), which

seems to confirm the slow logarithmic growth law mentioned before.

Discussion of the rejuvenation effect is slightly more subtle. It is indeed not yet obvious that the effect as it is observed in computer simulations and reported, for example, in Fig. 22, is exactly similar to the one observed in experiments. The difficulty comes from the fact that some seemingly innocuous details of the experimental protocol, such as the necessary use in experiments of finite cooling rates, in fact play a crucial role and influence the physics so that direct comparison between experiments and simulations is difficult. In numerical work, rejuvenation can be attributed to a gradual change with temperature of the nature of spatial correlations between spins that develop with time (Berthier and Young 2005; Berthier and Bouchaud 2002). More drastic changes are predicted to occur in disordered systems as a result of the chaotic evolution with temperature of the metastable states in a spin glass (so-called chaos effect (Bray and Moore 1987)), which could also be responsible for the observed rejuvenation effect (Jönsson et al. 2004).

Mean-Field Aging and Effective Temperatures

Theoretical studies of mean-field glassy models have provided important insights into the aging dynamics of both structural and spin glasses (Cugliandolo and Kurchan 1993, 1994). Although such models are defined in terms of spin degrees of freedom interacting via infinite-ranged interactions, the deep connections between them and the mode-coupling theory of the glass transition make them serious candidates to investigate glassy states in general, not only thermodynamic properties at thermal equilibrium but also nonequilibrium aging dynamics. Despite their often reported “simplicity,” it took several years to derive a proper asymptotic solution of the long-time dynamics for a series of mean-field spin glasses (see Cugliandolo in Barrat et al. (2004)). These results have then triggered an enormous activity (Crisanti and Ritort 2003) encompassing theoretical, numerical, and also experimental work trying to understand further these results, and to check in more realistic systems whether they have some reasonable range of applicability beyond mean-field.

This large activity, by itself, easily demonstrates the broad interest of these results. More recently, the derivation of the static properties of liquids and glasses in large dimensions has renewed the interest in mean-field dynamic phenomena (Parisi et al. 2020). In particular, the dynamic equations governing the equilibrium properties of supercooled liquids have now been derived (Maimbourg et al. 2016; Kurchan et al. 2016) and their consequences are being explored (Manacorda et al. 2020). The study of the nonequilibrium (aging and sheared) dynamics is now under way (Agoritsas et al. 2018, 2019; Altieri et al. 2020).

In these mean-field models, thermal equilibrium is never reached, and aging proceeds by downhill motion in an increasingly flat free energy landscape (Kurchan and Laloux 1996), with subtle differences between spin glass and structural glass models. In both cases, however, time translational invariance is broken, and two-time correlation and response functions depend on both their temporal arguments. In fact, the exact dynamic solution of the equations of motion for time correlators displays behaviors in strikingly good agreement with the numerical results reported in Fig. 21.

In these systems, the equations of motion in the aging regime involve not only temporal correlations, but also time-dependent response functions. At thermal equilibrium, response and correlation are not independent, since the fluctuation-dissipation theorem (FDT) relates both quantities. In aging systems, there is no reason to expect the FDT to hold and both quantities carry, at least in principle, distinct physical information. Again, the asymptotic solution obtained for mean-field models quantitatively establishes that the FDT does not apply in the aging regime. Unexpectedly, the solution also shows that a generalized form of the FDT holds at large waiting times (Cugliandolo and Kurchan 1993). This is defined in terms of the two-time connected correlation function for some generic observable $A(t)$,

$$C(t, t_w) = \langle A(t)A(t_w) \rangle - \langle A(t) \rangle \langle A(t_w) \rangle, \quad (42)$$

with $t \geq t_w$, and the corresponding two-time (impulse) response function

$$R(t, t_w) = T \left. \frac{\delta \langle A(t) \rangle}{\delta h(t_w)} \right|_{h=0}. \quad (43)$$

Here h denotes the thermodynamically conjugate field to the observable A so that the perturbation to the Hamiltonian (or energy function) is $\delta E = -hA$, and angled brackets indicate an average over initial conditions and any stochasticity in the dynamics. Note that we have absorbed the temperature T in the definition of the response, for convenience. The associated generalized FDT reads then

$$R(t, t_w) = X(t, t_w) \frac{\partial}{\partial t_w} C(t, t_w), \quad (44)$$

with $X(t, t_w)$ the so-called fluctuation-dissipation ratio (FDR). At equilibrium, correlation and response functions are time translation invariant, depending only on $\tau = t - t_w$, and equilibrium FDT imposes that $X(t, t_w) = 1$ at all times. A parametric fluctuation-dissipation (FD) plot of the step response or susceptibility

$$\chi(t, t_w) = \int_{t_w}^t dt' R(t, t'), \quad (45)$$

against

$$\Delta C(t, t_w) = C(t, t) - C(t, t_w), \quad (46)$$

is then a straight line with unit slope. These simplifications do not occur in nonequilibrium systems. But the definition of an FDR through Eq. (44) becomes significant for aging systems (Cugliandolo and Kurchan 1993, 1994). In mean-field spin glass models the dependence of the FDR on both temporal arguments is only through the correlation function,

$$X(t, t_w) \sim X(C(t, t_w)), \quad (47)$$

valid at large waiting times, $t_w \rightarrow \infty$. For mean-field structural glass models, the simplification (47) is even more spectacular since the FDR is shown to be characterized by only two numbers instead of a function, namely $X \sim 1$ at short times (large

value of the correlator) corresponding to a quasi-equilibrium regime, with a crossover to a non-trivial number, $X \sim X^\infty$ for large times (small value of the correlator). This implies that parametric FD plots are simply made of two straight lines with slope 1 and X^∞ , instead of the single straight line of slope 1 obtained at equilibrium.

Since any kind of behavior is in principle allowed in nonequilibrium situations, getting such a simple, equilibrium-like structure for the FD relations is a remarkable result. This immediately led to the idea that aging systems might be characterized by an effective thermodynamic behavior and the idea of quasi-equilibration at different timescales (Cugliandolo et al. 1997). In particular, generalized FD relations suggest to define an effective temperature, as

$$T_{\text{eff}} = \frac{T}{X(t, t_w)}, \quad (48)$$

such that mean-field glasses are characterized by a unique effective temperature, $T_{\text{eff}} = T/X^\infty$. It is thought of as the temperature at which slow modes are quasi-equilibrated. One finds in general that $0 < X^\infty < 1$, such that $T_{\text{eff}} > T$, as if the system had kept some memory of its high temperature initial state.

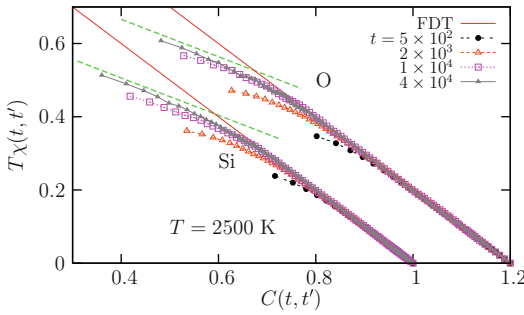
The name “temperature” for the quantity defined in Eq. (48) is not simply the result of a dimensional analysis but has a deeper, physically appealing meaning that is revealed by asking the following questions. How does one measure temperatures in a many-body system whose relaxation involves well-separated timescales? What is a thermometer (and a temperature) in a far from equilibrium aging material? Answers are provided in Cugliandolo et al. (1997), and Kurchan (2005) both for mean-field models and for additional toy models with multiple relaxation timescales. The idea is to couple an additional degree of freedom, such as a harmonic oscillator, $x(t)$, which plays the role of the thermometer operating at frequency w , to an observable of interest $A(t)$ via a linear coupling, $-\lambda x(t)A(t)$. Simple calculations show then that the thermometer “reads” the following temperature,

$$\frac{1}{2} K_B T_{\text{meas}}^2 = \frac{1}{2} \omega^2 \langle x^2 \rangle = \frac{\omega C'(\omega, t_w)}{2\chi''(\omega, t_w)}, \quad (49)$$

where $C'(\omega, t_w)$ is the real part of the Fourier transform of Eq. (42), and $\chi(\omega, t_w)$ the imaginary part of the Fourier transform of Eq. (43), with $h = \lambda x$. The relation (49) indicates that the bath temperature is measured, $T_{\text{meas}} = T$, if the frequency is high and FDT is satisfied, while $T_{\text{meas}} = T_{\text{eff}} > T$ if the frequency is slow enough to be tuned to that of the slow relaxation in the aging material. The link between the FDR in Eq. (44) and the effective temperature measured in Eq. (49) was numerically confirmed in the computer simulation of a glassy molecular liquid in Berthier and Barrat (2002a).

More generally, relaxation in glassy systems occurs in well-separated time sectors (Cugliandolo and Kurchan 1994); it is then easy to imagine that each sector could be associated with an effective temperature (Kurchan 2005). A thermodynamic interpretation of effective temperatures has also been put forward, relating them to the concept of replica symmetry breaking (Franz et al. 1998). Interestingly, the full-step or one-step replica symmetry breaking schemes needed to solve the static problem in these models have a counterpart as the FDR being a function or a number, respectively, in the aging regime. Moreover, we note that these modern concepts are related to, but make much more precise, older ideas of quasi-equilibrium and fictive temperatures in aging glasses (Struik 1977).

Taken together, these results make the mean-field description of aging very appealing, and they nicely complement the mode-coupling/RFOT description of the equilibrium glass transition described above. Moreover, they have set the agenda for a large body of numerical and experimental work, as reviewed in Crisanti and Ritort (2003). In Fig. 23 we present recent numerical data obtained in an aging silica glass (Berthier 2007b), presented in the form of a parametric response-correlation plot. The measured correlation functions are the self-part of the intermediate scattering functions defined in Eq. (5), while the conjugated response functions quantify the



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 23 Parametric correlation-response plots measured in the aging regime of a numerical model for a silica glass, SiO_2 (Berthier 2007b). The plots for both species smoothly converges toward a two-straight line plot of slope 1 at short times (large C values), and of slope $X^\infty \approx 0.51$ at large times (small values of C), yielding an effective temperature of about $T_{\text{eff}} = T/X^\infty \approx 4900$ K. Note that the glass transition temperature of SiO_2 is 1446 K

response of particle displacements to a spatially modulated field conjugated to the density. Plots for silicon and oxygen atoms at different ages are presented. They seem to smoothly converge toward a two-straight line plot, as obtained in mean-field models (note, however, that this could be just a pre-asymptotic, finite “ t_w ,” effect). Moreover, the second, nontrivial part of the plot is characterized by a slope that appears to be independent of the species, and of the wavevector chosen to quantify the dynamics, in agreement with the idea of a unique asymptotic value of the FDR, possibly related to a well-defined effective temperature.

Beyond Mean-Field: Real Space

Despite successful results, such as those shown in Fig. 23, the broader applicability of the mean-field scenario of aging dynamics remains still unclear. While some experiments and simulations indeed seem to support the existence of well-behaved effective temperatures (Grigera and Israeloff 1999; Abou and Gallet 2004; Wang et al. 2006), other studies also reveal the limits of the mean-field scenario. Experiments have for instance reported anomalously large FDT violations associated with intermittent dynamics (Bellon et al. 2001; Bellon and Ciliberto 2002; Buisson et al. 2003a, b), while theoretical studies of model systems have also

found non-monotonic or even negative response functions (Talbot et al. 2003; Nicodemi 1999; Krzaka 2005; Depken and Stinchcombe 2005), and ill-defined or observable-dependent FDRs (Fielding and Sollich 2002). In principle, these discrepancies with mean-field predictions are to be expected, since there are many systems of physical interest in which the dynamics are not of mean-field type, displaying both activated processes and spatial heterogeneity.

It is thus an important task to understand from the theoretical point of view when the mean-field concept of an FDR-related effective temperature remains viable. However, theoretically studying the interplay between relevant dynamic lengthscales and thermally activated dynamics in the nonequilibrium regime of disordered materials is clearly a challenging task. Nevertheless, this problem has been approached in different ways, as we briefly summarize in this subsection.

A first class of system that displays aging and spatial heterogeneity is given by coarsening systems. The paradigmatic situation is that of an Ising ferromagnetic model (with a transition at T_c) suddenly quenched in the ferromagnetic phase at time $t_w = 0$. For $t_w > 0$, domains of positive and negative magnetizations appear and slowly coarsen with time. The appearance of domains that grow with time proves the presence of both aging and heterogeneity.

The case where the quench is performed down to $T < T_c$ is well understood. The system becomes scale invariant (Bray 1994), since the only relevant lengthscale is the growing domain size, $\ell(t_w)$. Correlation functions display aging, and scale invariance implies that $C(t, t_w) \sim f(\ell(t)/\ell(t_w))$. Response functions can be decomposed into two contributions (Barrat 1998; Berthier et al. 1999): one part stems from the bulk of the domains and behaves as the equilibrium response, and a second one from the domain walls and becomes vanishingly small in the long time limit, where $\ell(t_w) \rightarrow \infty$ and the density of domain walls vanishes. This implies that for coarsening systems in $d \geq 2$, one has $X^\infty = 0$, or equivalently an infinite effective temperature, $T_{\text{eff}} = \infty$. The case $d = 1$ is special because $T_c = 0$ and the response function remains dominated by the domain walls, which yields the

nontrivial value $X^\infty = 1/2$ (Godr che and Luck 2000; Lippiello and Zannetti 2000).

Another special case has retained attention. When the quench is performed at $T = T_c$, there is no more distinction between walls and domains and the above argument yielding $X^\infty = 0$ does not hold. Instead one studies the growth of critical fluctuations with time, with $\xi(t_w)t_w^{1/z}$ the correlation length at time t_w , where z is the dynamic exponent. Both correlation and response functions become nontrivial at the critical point (Godr che and Luck 2000). It proves useful in that case to consider the dynamics of the Fourier components of the magnetization fluctuations, $C_q(t, t_w) = \langle m_q(t)m_{-q}(t_w) \rangle$, and the conjugated response $R_q(t, t_w) = \frac{\delta \langle m_q(t) \rangle}{\delta h_{-q}(t_w)}$. From Eq. (44) a wave-vector-dependent FDR follows, $X_q(t, t_w)$, which has interesting properties (Mayer et al. 2003) (see Calabrese and Gambassi (2005) for a review).

In dimension $d = 1$, it is possible to compute $X_q(t, t_w)$ exactly in the aging regime at $T = T_c = 0$. An interesting scaling form is found, and numerical simulations performed for $d > 1$ confirm its validity:

$$X_q(t, t_w) = \chi(q^2 t_w), \quad (50)$$

where the scaling function $\chi(x)$ is $\chi(x \rightarrow \infty) \rightarrow 1$ at small lengthscale, $q\xi \gg 1$, and $\chi(x \rightarrow 0) \rightarrow 1/2$ (in $d = 1$) at large distance, $q\xi \ll 1$; recall that $z = 2$ in that case.

Contrary to mean-field systems where geometry played no role, here the presence of a growing correlation lengthscale plays a crucial role in the off-equilibrium regime since $\xi(t_w)$ allows one to discriminate between fluctuations that satisfy the FDT at small lengthscale, $X_q \sim 1$, and those at large lengthscale which are still far from equilibrium, $0 < X_q \sim X^\infty < 1$. These studies suggest therefore that generalized fluctuation-dissipation relations in fact have a strong lengthscale dependence – a result which is not predicted by mean-field approaches.

Another interesting result is that the FDT violation for global observables (i.e., those at $q = 0$) takes a particularly simple form, since the introduction of a single number is sufficient, the FDR

at zero wavevector, $X_q = 0(t, t_w) = X^\infty = 1/2$ (in $d = 1$). This universal quantity takes nontrivial values in higher dimension, for example, $X^\infty \approx 0.34$ is measured in $d = 2$ (Mayer et al. 2003). This shows that the study of global rather than local quantities makes the measurement of X^∞ **much** easier. Finally, having a nontrivial value of X^∞ **for** global observables suggests that the possibility to define an effective temperature remains valid, but it has become a more complicated object, related to global fluctuations on large lengthscale.

Kinetically constrained spin models represent a second class of non-mean-field systems whose off-equilibrium has been thoroughly studied recently (L onard et al. 2007). This is quite a natural thing to do since these systems have local, finite ranged interactions, and they combine the interesting features of being defined in terms of (effective) microscopic degrees of freedom, having local dynamical rules, and displaying thermally activated and heterogeneous dynamics.

The case of the Fredrickson-Andersen model, described in section “[Theory of the Glass Transition](#),” has been studied in great detail (L onard et al. 2007), and we summarize the main results. Here, the relevant dynamic variables are the Fourier components of the mobility field, which also correspond in that case to the fluctuations of the energy density. Surprisingly, the structure of the generalized fluctuation-dissipation relation remains once more very simple. In particular, in dimension $d > 2$, one finds a scaling form similar to (50), $X_q(t, t_w) = \chi(q^2 t_w)$, with a well-defined limit at large distance $X_{q=0}(t, t_w) = X^\infty$. The deep analogy with critical Ising models stems from the fact that mobility defects in KCMs diffuse in a way similar to domain walls in coarsening Ising models. It is in fact by exploiting this analogy that analytic results are obtained in the aging regime of the Fredrickson-Andersen model (Mayer and Sollich 2007).

There is however a major qualitative difference between the two families of model. The (big!) surprise lies in the sign of the asymptotic FDR, since calculations show that (Mayer et al. 2006)

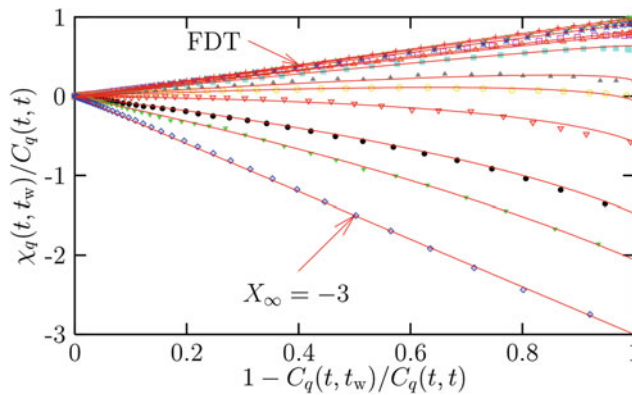
$$X^\infty = -3, d > 2. \quad (51)$$

In dimension $d = 1$, one finds $X_q = 0(t, t_w) = f(t/t_w)$ with $X_{q=0}(t \rightarrow \infty, t_w) = \frac{3\pi}{16-6\pi} \approx -3.307$. Numerical simulations confirm these calculations. In Fig. 24, we show such a comparison between simulations (symbols) and theory (lines) in the case of the $d = 3$ Fredrickson-Andersen model (Mayer et al. 2006). Fourier components of the mobility field yield parametric FD plots that follow scaling with the variable $q^2 t_w$, as a direct result of the presence of a growing lengthscale for dynamic heterogeneity, $\xi(t_w) \sqrt{t_w}$. Again, generalized fluctuation-dissipation relations explicitly depend on the spatial lengthscale considered, unlike in mean-field studies. In Fig. 24, the limit $q = 0$ corresponding to global observables is also very interesting since the plot is a pure straight line, as in equilibrium. Unlike equilibrium, however, the slope is not 1 but -3 . A negative slope in this plot means a negative FDR, and therefore suggests a negative effective temperature, a very nonintuitive result at first sight.

Negative response functions in fact directly follows from the thermally activated nature of the dynamics of these models (Mayer et al. 2006). First, one should note that the global observable shown in Fig. 24 corresponds to fluctuations of the energy, $e(t_w)$, whose conjugated

field is temperature. In the aging regime the system slowly drifts toward equilibrium. Microscopic moves result from thermally activated processes, corresponding to the local crossing of energy barriers. An infinitesimal change in temperature, $T \rightarrow T + \delta T$ with $\delta T > 0$, accelerates these barrier crossings and makes the relaxation dynamics faster. The energy response to a positive temperature pulse is therefore negative, $\delta e < 0$, which directly yields $\delta e / \delta T < 0$, which explains the negative sign of the FDR. This result does not hold in mean-field glasses, where thermal activation plays no role.

Finally, another scenario holds for local observables in some KCMs when kinetic constraints are stronger, such as the East model (Léonard et al. 2007) or a bidimensional triangular plaquette model (Jack et al. 2006b). Here, relaxation is governed by a hierarchy of energy barriers that endow the systems with specific dynamic properties. In the aging regime following a quench, in particular, the hierarchy yields an energy relaxation that arises in discrete steps which take place on very different timescales, reminiscent of the “time sectors” encountered in mean-field spin glasses. Surprisingly, it is found that to each of these discrete relaxations one can associate a well-defined (positive) value of the fluctuation-dissipation ratio, again reminiscent of



Glasses and Aging, A Statistical Mechanics Perspective on, Fig. 24 Parametric response-correlation plots for the Fourier components of the mobility field in the $d = 3$ Fredrickson-Andersen model. Symbols are from simulations, lines from analytic calculations, and wavevectors decrease from top to bottom. The FDT is close to being

satisfied at large q corresponding to local equilibrium. At larger distance deviations from the FDT are seen, with an asymptotic FDR which becomes negative. Finally, for energy fluctuations at $q = 0$ (bottom curve), the plot becomes a pure straight line of (negative!) slope -3 , as a result of thermally activated dynamics

the dynamics of mean-field spin glass models. Therefore, a physical picture seems to have some validity, even in models that are very far from the mean-field limit: in that picture, slow relaxation takes place on multiple timescales, with each timescale characterized by a different effective temperature.

Beyond Mean-Field: Energy Landscape

What the mean-field approach crucially lacks is the description of activated processes that allow the system to jump over larger and larger barriers at large times. One way to introduce this key effect is to study mean-field models at finite system size N . In fact, the mean field theory of aging is derived by first taking the limit $N \rightarrow \infty$ to study the dynamics on large but finite timescales. Instead, if one focuses on timescales that diverge exponentially with N , activated processes will occur. One can then analyze in a controlled way how jumping over barriers alters the mean-field dynamics.

This approach was pioneered numerically by Crisanti and Ritort (2000a; b, 2003), and more recently pursued further in (Baity-Jesi et al. 2018a, b; Billoire et al. 2005; Stariolo and Cugliandolo 2019). One of the most important outcomes of their study is to show the existence of an effective temperature and its relation with the energy landscape, more precisely the complexity, even when barriers are crossed. The understanding of the dynamical evolution in this regime was reached recently by theoretical and rigorous analysis of the Random Energy Model (REM) in (Baity-Jesi et al. 2018a; Baity-Jesi et al. 2018b; Arous et al. 2002; Gayraud 2019). It was shown that when observing the dynamics on exponentially large (in N) timescales, activated processes lead to a dynamical evolution that can be mapped on the one of the trap model (Bouchaud 1992; Dyre 1987). Again, an interesting relation with the energy landscape emerges: the exponent of the trapping time power law describing aging dynamics at a given energy is directly linked to the slope of the configurational entropy at that energy. It is not yet clear whether this scenario goes beyond the REM and applies, for instance, to the Monte Carlo dynamics of the p -spin model. In this case the energy landscape is

more complex and one needs to understand the interplay between energy and entropic barriers (Barrat and Mézard 1995; Cammarota and Marinari 2015, 2018).

To this end, a series of recent works focused on the organization in configuration space of the barriers that can be used to escape from a given minimum for the p -spin spherical model. By using the Kac-Rice formalism, these works computed the entropy of the barriers at a given energy and at a certain distance from a given minimum (Ros et al. 2019) and obtained the dynamical instanton representing the escape from a given minimum.

Finally, another set of works performed a complementary study on finite size models of three dimensional supercooled liquids. The key idea was to focus on a size that is large enough to be representative of the bulk behavior and small enough to be able to study the dynamics in terms of energy landscape (Büchner and Heuer 1999; Doliwa and Heuer 2003; Heuer 2008). This led to the introduction of the notion of metabasins, a set of basins that corresponds to the same metastable state. A study of the dynamics in terms of energy barriers between metabasins was then performed. It showed in a very compelling way that the dynamics start to be activated even above the MCT cross-over in 3D systems (Doliwa and Heuer 2003; Denny et al. 2003). Interestingly, a strong relationship with the dynamics of the trap model was also found in this case (Heuer 2008).

All the results cited above provide valuable information and insights on activated dynamics. Interestingly, they show that relations between aging dynamics and energy landscape found within mean-field theory seem to hold more broadly. Many questions remain open and will hopefully be addressed in future work, such as understanding and characterizing the dynamical paths and the barrier crossings leading to relaxation during the aging regime.

Driven Glassy Materials

We have introduced aging phenomena with the argument that in a glass phase, the timescale to equilibrate becomes so long that the system always remembers its complete history. This is true in general, but one can wonder whether it is

possible to invent a protocol where the material history could be erased, and the system “rejuvenated” (McKenna and Kovacs 1984). This concept has been known for decades in the field of polymer glasses, where complex thermo-mechanical histories are often used.

Let us consider an aging protocol where the system is quenched to low temperature at time $t_w = 0$, but the system is simultaneously forced by an external mechanical constraint. Experimentally one finds that a stationary state can be reached, which explicitly depends on the strength of the forcing: a system which is forced more strongly relaxes faster than a material that is less solicited, a phenomenon called “shear-thinning.” The material has therefore entered a driven steady state, where memory of its age is no longer present and the dynamics have become stationary: aging is stopped.

Many studies of these driven glassy states have been performed in recent years. These studies are relevant for the rheology of supercooled liquids and glasses, and the $T \ll T_g$ limit corresponds to studies of the plasticity of amorphous solids, a broad field in itself, see section “Rheology.” In the colloidal world, such studies are also relevant for the newly-defined field of the rheology of “soft glassy materials.” These materials are (somewhat tautologically) defined as those for which the nonlinear rheological behavior is believed to result precisely from the competition between intrinsically slow relaxation processes and an external forcing (Sollich et al. 1997; Ikeda et al. 2012). It is believed that the rheology of dense colloidal suspensions, foams, emulsions, binary mixtures, or even biophysical systems is ruled by such a competition, which represents a broad scope for applications.

From the point of view of statmech modeling, soft glassy rheology can be naturally studied from the very same angles as the glass transition itself. As such trap models (Sollich et al. 1997; Sollich 1998), mean-field spin glasses (Berthier et al. 2000), and the related mode-coupling theory approach (Miyazaki and Reichman 2002; Fuchs and Cates 2002) have been explicitly extended to include an external mechanical forcing. In all these cases, one finds that a driven steady state can be reached and aging is indeed expected to

stop at a level that depends on the strength of the forcing. Many of the results obtained in aging systems about the properties of an effective temperature are also shown to apply in the driven case, as shown both theoretically (Berthier et al. 2000) and numerically (Berthier and Barrat 2002b). A most interesting aspect is that the broad relaxation spectra predicted to occur in glassy materials close to a glass transition directly translate into “anomalous” laws both for the linear rheological behavior (seen experimentally in the broad spectrum of elastic, $G'(\omega)$ and loss, $G''(\omega)$, moduli), and the nonlinear rheological behavior (a strong dependence of the viscosity η upon the shear rate $\dot{\gamma}$).

Future Directions

The problem of the glass transition, already very exciting in itself, has ramifications well beyond the physics of supercooled liquids. Glassy systems figure among the even larger class of “complex systems.” These are formed by a set of interacting degrees of freedom showing nontrivial emergent behavior: as a whole they exhibit properties that are not already encoded in the definition of the individual parts. As a consequence the study of glass-formers as statistical mechanics models characterized by frustrated interactions is a fertile ground to develop new concepts and techniques that will likely be applied to other physical, and more generally, scientific situations.

An example, already cited in this review, is the progress obtained in computer science and information theory (Bouchaud et al. 2011) using techniques originally developed for spin glasses and structural glasses. There is no doubt that progress will steadily continue in the future along these interdisciplinary routes. Concerning physics, glassiness is such a ubiquitous and, yet as we showed, rather poorly understood problem that many developments are very likely to take place in the next decade.

Instead of guessing future developments of the field (and then very likely be proven wrong), we prefer to list a few problems we would like to see solved in the next years.

- Is the glass transition related to a true phase transition? If yes, a static or a dynamic one? A finite or zero temperature one?
- Do RFOT theory, defects models, or frustration-based theory form the correct starting points of “the” theory of the glass transition?
- Is MCT really a useful theory for the first decades of slowing down of the dynamics? Can one find direct evidence that an avoided MCT transition exists and controls the dynamics?
- What is the correct physical picture for the low temperature phase of glass-forming liquids and spin glasses?
- Are there general principles governing off-equilibrium dynamics, and in particular aging and sheared materials?
- Do non-disordered, finite-dimensional, and finite-range statmech model exist that display a thermodynamically stable amorphous phase at low temperature?

Finally, notice that we did not discuss possible interplays between glassiness, disorder, and quantum fluctuations. This is a very fascinating topic that has boomed in recent years; new phenomena such as Many-Body Localization (Nandkishore and Huse 2015) and Quantum Scars (Turner et al. 2018) have been discovered, revealing new facets of slow dynamics. Models of classical glasses, such as the KCMs and the p-spin models, found new applications in this arena (Pancotti et al. 2020; Facoetti et al. 2019).

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Stress Localization in Soft Particulate Gels

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Article Outline

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Glossary

Gels Refers to solid-like materials composed by an interconnected matrix embedded in a solvent. The matrix can be made by cross-linked polymers that constitute a network in polymer gels or particulate matter that further self-assembles into a solid, porous matrix in other cases. Particulate gels are also referred to as **colloidal gels** when made of colloidal units, that is, particles or aggregates that have sizes from $\sim 10\text{nm}$ to $\sim 1\mu\text{m}$.

Stress Refers to the force per unit area across a plane that goes through a material. Internal stresses result from the forces between the microscopic components of the material, in response to an external deformation or changing environmental conditions. In elastic

solids, external stresses produce a deformation associated to energy stored by adjusting the forces between the microscopic components.

Elasticity Refers to the capacity of a solid material to store energy when subjected to a deformation or a load. The elastic modulus quantifies the deformation that the solid material can accommodate, by storing energy, when subjected to an external load; or the amount of energy per unit volume that can be stored when subjected to a deformation and that translates into an increase of stress.

Rigidity Refers to a solid structure that is mechanically stable, has a finite elastic modulus, and hence can support an external load without flowing or yielding.

Definition of the Subject

Many materials we eat, spread, squeeze, or 3D print are gels, soft amorphous solids whose solid component is constituted by a network of self-assembled particles or agglomerated smaller units (proteins, polymers, or other particulates). The properties and mechanical performance of these gels are determined by a complex interplay between the molecular cohesion or surface interactions in the solid component, the aggregation kinetics that drive formation of various types of structures, and the effect of external forces that can promote breaking or reforming of the solid network. Solidification processes are typically sources of frozen-in stresses in the load bearing network and help build a memory of the processing history in these amorphous solids. Moreover, the disorder in the stress-bearing structure promotes and enhances stress localization under load. The feedback between stress heterogeneities, structural disorder, and nonequilibrium conditions is therefore key to the mechanical response of these fascinating and ubiquitous materials.

Introduction

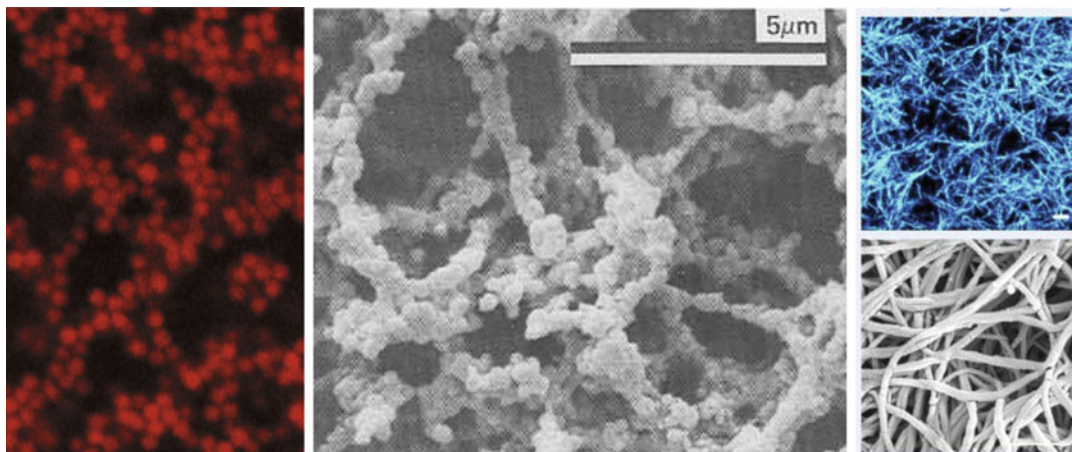
Materials made from polymers, colloidal suspensions and surfactants, are at the core of novel technologies that require tunable mechanics. In many cases, these soft and adaptive solids are *gels*, that is, they are prevalently composed of a fluid in which a relatively small amount (sometimes tiny!) of solid material is embedded. The key is that the solid component, typically made of small particles or aggregates, is spatially organized into an open, porous network and hence, in spite of being the minority constituent, is able to provide rigidity and control the mechanical response of the whole material. Gels are ubiquitous in nature, probably because they provide the means to optimize mechanical functionalities without necessarily blocking transport or diffusion of various substances, while they require in principle arbitrarily small amounts of solid matter. In the biological context, it is clear that their highly adaptive and tunable rheological response is central to biological functions. For technological applications, because of the sparse and in many case reconfigurable solid matrix embedded in the fluid, they can flow, be stretched, squeezed, or fractured. The small amount of actual solid material needed makes them also extremely convenient to include new high-value functional components while limiting costs and risks.

For gels obtained through polymerization reactions or crosslinking of polymer solutions, polymer physics provides the basis to understand their rheology (de Gennes 1979; Rubinstein and Colby 2003). The elasticity is largely entropic in nature in these materials, like in rubber, and can be tuned mainly by varying the density of crosslinks or of the reacting units, which is the main control parameter in the gelation process. Connectivity is the key because thermal fluctuations guarantee an elastic response as long as there is a connected path through the sample. The formation of such connected path is, in most cases, described by a random percolation process, because the functional units that react to create the gel network are typically uniformly distributed in space and their chemical reactions or physical associations are the limiting process (Stauffer et al. 1982).

Particulate gels can form, instead, through a number of complex (and sometimes hierarchical) physical processes initiated by the net interactions in solution of colloidal (supramolecular) units, which lead to a self-assembled spanning solid-like matrix (Del Gado et al. 2016). The colloidal units relevant to the gel build-up can be the result of specifically designed chemical synthesis (i.e., nanoparticles, microgel particles), of aggregation or hierarchical self-assembly of smaller units (i.e., flocs, micelles, fibrils), or of conformational changes of polymers and biopolymers (Fig. 1). Hence, these (colloidal) particulate gels are relevant to quite a wide range of systems in soft matter, from proteins to other biopolymers, clay materials, and cement, to ceramics and to polymer-based or microgel materials.

The wide range of physical chemistry at play and the lack of a coherent theoretical framework analogue to polymer physics make it much more challenging to identify common traits and unifying physical concepts that help understand and predict the mechanics. While these materials can be extremely soft because of the overall low solid content, the strength of the interactions that drive the aggregation of the colloidal units into the gel network must be large enough with respect to $k_B T$ to overcome thermal fluctuations and stabilize the gel structural elements and their connections. The implication is that the elasticity here is largely enthalpic in nature and that the interaction strength, together with the total volume fraction of the solid content, controls elastic moduli, viscoelastic spectra, and nonlinear response. Remarkably, the interaction strength alone does not allow to predict the gel properties: the morphology of the gel networks, its structural elements and their connectivity, may change a lot due to different kinetics at play during the gel self-assembly, leading to huge variations of the mechanical response, sometimes even for similar compositions of the initial solution.

Considering the nature of the aggregation processes is therefore crucial in these materials, and not only because these processes change the gel morphology and appearance, but also, and probably more importantly, because they provide insight into how local stresses and mechanical



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Fig. 1 Solid networks in soft particulate gels. Left: colloidal particles in a colloidal gel from (Whitaker et al. 2019). Reprinted with permission. Creative Commons license available at <https://creativecommons.org/licenses/by/4.0/>. Center: SEM image of casein gels which are the

basis of yogurt products ((Kalab et al. 1983). Reprinted with permission. Creative Commons license available at <https://creativecommons.org/licenses/by/4.0/>). Right (top and bottom): Confocal reflectance images of gels of collagen fibrils obtained at different temperatures from (Burla et al. 2020).

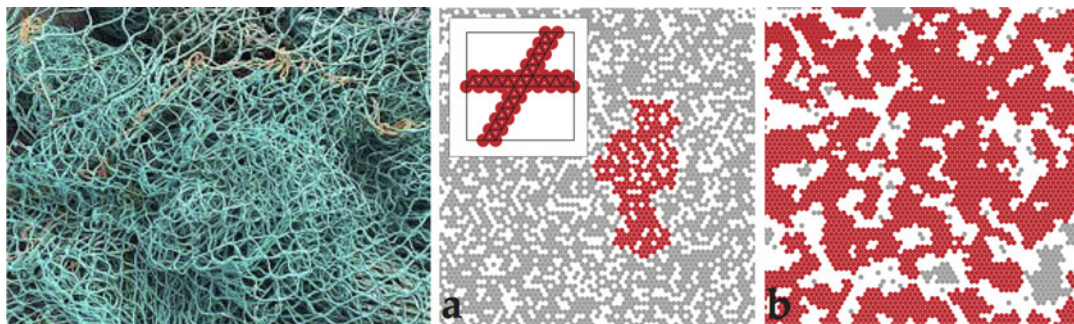
heterogeneities get embedded and remain frozen-in, in the gel structure, during gelation. As in a wide range of soft amorphous solids, there is growing evidence that the mechanical response of these soft gels emerges from localized stress patterns with nontrivial geometry (Nampoothiri et al. 2020). Furthermore, due to the predominantly enthalpic nature of the gel networks, thermal fluctuations play a much reduced role in the elasticity, and connectivity through the sample is not sufficient to guarantee a solid-like, elastic response (Fig. 2).

Large colloidal aggregates can be still non-rigid, just like a floppy but fully connected fishing net, and a *rigid* percolating backbone, satisfying the constraints of mechanical equilibrium, must be present for a solid-like response to emerge. Therefore, while microscopy and spectroscopy imaging techniques often provide quantitative and multiscale insight into the morphology of the aggregates that compose the gel, one still needs to combine it with information on the topology of the larger scale particle assemblies and on the forces that act as mechanical constraints on the gel units, to gain access to the part of the structure that is rigid and load-bearing.

Different aggregation paths, that can become available by varying the gelation conditions, can

favor or not the development of various types of mechanical heterogeneities, where rigid structures coexist with, or are interspersed in, floppy or softer regions. The presence of such mechanical heterogeneities, often not recognizable from structural and morphological heterogeneities, translates into stress and strain localization when the material is deformed or under load, or into prestressed states that will evolve due to thermal fluctuations, under deformation or changing boundary conditions. The understanding of the emergence of rigidity and of the role of stress localization in the mechanics of particulate gels has just started, but it is clearly key to designing and expanding their performances and functions.

The remainder of the chapter tries to provide an overview of the fundamental physics understanding of these soft particulate gels, and in particular of how stress localization emerges as the central ingredient controlling their mechanics, in spite of the softness and deformability of these materials. I start by discussing briefly how microstructural heterogeneities can emerge during gelation, promoting frozen-in stresses in section “[Source of Mechanical Heterogeneities and Frozen-in Stresses: Microscopic Forces and Gelation Processes](#).” Microscopic processes and heterogeneities



Stress Localization in Soft Particulate Gels, Fig. 2 Connectivity and rigidity in soft gels. Left: A connected mesh can be floppy in absence of thermal fluctuations. Center and right: self-assembled structures in a simple 2D model for colloidal gels (Reprinted with

permission from (Zhang et al. 2019)): rigid structures (red) can constitute a minor portion of the percolating connected nonrigid (gray) cluster, depending on the aggregation path.

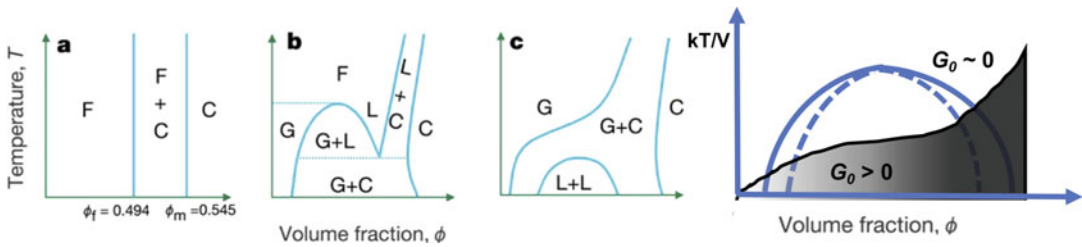
enter rigidity and elasticity, as briefly outlined in section “[Origin of Elastic Modulus and Emergence of Rigidity](#).” Section “[Stress Localization at Rest and Under Shear](#)” gives a concise account of ideas for microscopic processes at rest and under an external load. Finally, section “[Future Directions](#)” contains an outlook of the outstanding questions and new research paths.

Source of Mechanical Heterogeneities and Frozen-in Stresses: Microscopic Forces and Gelation Processes

In soft particulate gels, gelation is typically initiated by the net physical interactions between the colloidal units in solution, which can be described through equilibrium statistical mechanics and thermodynamics. However, the final result, in terms of solid matrix, is a nonequilibrium, nonergodic state that depends on the path along which the system evolves given the procedure used (e.g., mixing, temperature control, etc.). The lengthscales over which nonergodic processes dominate depend on the physical chemistry at play, but also on procedures and conditions, and determine the type of frozen-in stresses and mechanical heterogeneities that are crucial to the gel mechanics.

In terms of microscopic forces, well-studied and relatively simple cases of solvent-mediated interactions in colloidal suspensions are those

described by DLVO (Derjaguin and Landau 1941; Verwey and Overbeek 1948; Israelachvili 2011) or depletion interactions theories (Asakura and Oosawa 1954), providing simple analytical forms for short-ranged attractive forces that depend only on the particle surface separation, and where the attractive strength is determined by the composition and physical chemistry of the solution. These theoretical approaches give excellent estimates of phase and even gelation boundaries in many cases (Poon et al. 1997; Anderson and Lekkerkerker 2002). Figure 3 (left) shows typical phase diagrams for colloidal suspensions (reproduced from (Anderson and Lekkerkerker 2002) with permission) indicating gas, liquid, and crystalline phases in which the colloidal component can be found. Gelation can then be initiated by equilibrium (or close-to-equilibrium) phenomena predicted on the basis of these short range attractive interactions, such as phase separation or spinodal decomposition (Gibaud et al. 2008; Lu et al. 2008). Microphase separation phenomena, typical of colloidal suspensions with competing short range attraction and longer range repulsion, can also initiate gel formation (Campbell et al. 2005; Sciortino et al. 2005; De Candia et al. 2006; Ciach et al. 2013; Zhuang et al. 2016; Ioannidou et al. 2016). In all these cases, the initial driving of the aggregation is the underlying thermodynamics, with equilibrium (or close to equilibrium) sampling of microstates underpinning the initial evolution of the



Stress Localization in Soft Particulate Gels,

Fig. 3 Phase behavior and gelation in colloidal solutions. Left: Phase diagrams for colloidal suspensions for colloidal hard spheres (a) and short range attractions (b,c) indicating gas (G), Fluid (F) and liquid (L), and crystalline phases (C). Reproduced with permission from (Anderson and Lekkerkerker 2002). Right: A possible rigidity line for

colloidal suspensions with short range attractive interactions (with kT/V the ratio between attraction strength V and thermal energy at temperature T), at low volume fractions and across the binodal/spinodal regions (respectively continuum and dashed lines). G_0 is the low frequency elastic modulus of the gel (see also Zaccone et al. 2009)

microscopic degrees of freedom. Theoretical predictions of the effective interactions therefore provide useful information on the initial steps of the aggregation and structural build-up.

Frustration in the growth of large scale structures, also combined with the slowing down of the microscopic dynamics due to the vicinity of glassy states, can eventually result in gel structures with solid-like properties. A possible gel-line, defined by measuring the onset of a finite elastic modulus, is sketched in Fig. 3 (right) for colloidal suspensions with short range attractive interactions, in the low volume fraction region, where phase separation and spinodal decomposition can occur. Structural arrest of the microscopic dynamics associated to the emergence of gels or glassy states in presence of short range attraction has been extensively studied (Manley et al. 2004; Mayer et al. 2008; Lu et al. 2008; Gibaud and Schurtenberger 2009; Conrad et al. 2010). The final gel microstructure, from the thickness of the gel branches to pore sizes and connectivity, will depend not only on the volume fraction of the particle component and the interaction strength but also on the way nonergodicity is attained. For example, gels initiated in the vicinity of the spinodal line associated to short range attractive interactions are characterized by thick dense branches with large pores, and the specific pore size distribution can vary depending on the specific path chosen to quench the solution in the spinodal region (Foffi et al. 2005; Testard et al. 2011; Zia et al. 2014), on hydrodynamic interactions, and on

the viscoelasticity of the interfaces (Tanaka 2000; Padmanabhan and Zia 2018). These factors will influence both the possible structural arrest of the microscopic dynamics of the colloidal units and the way in which the internal stresses, that develop from the frustration at larger lengthscales as the gel forms, can be relaxed. As a consequence, they will determine the stress state of the gel, that is, the presence and nature of frozen-in stresses, and the spatial organization of local stresses in the gel structure. While different scenarios of kinetic arrest competing with phase separation and spinodal decomposition have been extensively discussed in the literature, the way they may control the final stress state of the gels has been highlighted in recent studies (Testard et al. 2011; Padmanabhan and Zia 2018; Filiberti et al. 2019; Tsurusawa et al. 2020) but is far from being fully understood.

Another aspect whose implications have been less investigated is that form and nature of surface forces in colloidal gels may be not necessarily captured by DLVO theories, for example, due to discreteness effects of ions and ion-water interactions that become important at small separations and in presence of high surface charges or multivalent ions (Shen and Bourg 2021; Goyal et al. 2021). Surface heterogeneity and roughness are also known to modify interaction strengths and sign (Monti et al. 2019). Moreover, once colloidal units are at close contact, different chemical or physical processes occurring on much smaller lengthscales, not included in existing theories, can drive the development of solid-on-solid contacts

and sintering of the particle surfaces (Bonacci et al. 2020).

As a consequence, the forces that are relevant to the formation of mechanical contacts during gelation may not simply depend on just the separation between surfaces of the colloidal units, but also on relative orientation of interparticle bonds or mechanical constraints, in the sense that the relative motion of particles in aggregates may be significantly more constrained than what spherically symmetric interactions would imply. It has been indeed shown experimentally that contacts between colloidal particles can resist torques (Pantina and Furst 2005; Wu et al. 2020) and that colloidal gels microstructures can be characterized by very low local coordination (Dinsmore et al. 2006; Dibble et al. 2008; Ohtsuka et al. 2008), supporting the idea that interparticle bonds may have bending resistance, that is, short range interactions may be directional and not only depend on interparticle separation (Del Gado and Kob 2005, 2010; Colombo and Del Gado 2014a; Bouzid and Del Gado 2020).

The implications are that the arrested structures and the micromechanics of the gels, may be qualitatively different from those obtained without considering these effects, even when the theoretical predictions for the phase boundaries can still provide useful indications of the regions of the phase diagram where gels will tend to form.

Interesting insights come from the studies of gelation in cases where one can access strong attractive forces between the colloidal units far enough from the spinodal or phase-separation boundaries. Gelation in colloidal suspensions has been investigated extensively for very low volume fractions of the solid components, for example, when the colloidal units are so dilute that can only interact if diffusing far enough, and only strong enough interactions can result in aggregation, which is therefore largely irreversible and results into fractal structures, typical of diffusion limited aggregation models (Lin et al. 1989; Trappe et al. 2001; Aime et al. 2018a; Cho et al. 2020). In these cases, gelation is obviously much less affected by the thermodynamics of the solution. If the aggregation is treated as irreversible, the kinetics is mostly limited to single

particle diffusion governed by the thermal fluctuations in the solvent, and a truly equilibrium sampling of the microstates of the particle assembly is not attained since it would require several aggregation- disaggregation steps. The implication is that the path through which the gel forms is nearly uniquely determined once particle volume fraction and diffusivity are fixed. Changing the initial conditions, as long as these properties are kept the same, may have very little impact on the gelation path. Hence the fact that gelation proceeds through exactly the same intermediate steps to the final gel state, with negligible effect of the initial conditions, is a direct manifestation of the non-equilibrium processes that drive it. In contrast, when equilibrium collective processes are entering the initial gel growth, changing the gelation path will significantly modify the gel obtained because it will correspond to different amounts of microstate sampling. In spite of these differences, the fact that irreversible aggregation requires interactions strengths dramatically larger than $k_B T$ could make the development of solid-on-solid contacts and surface interactions leading to noncentral forces also relevant here. In the case of irreversible aggregation, the fractal dimension of the aggregates can be modified by details of the surface interactions, such as the directionality and bending stiffness of interparticle bonds (Witten et al. 2004).

As particle density increases, the limiting diffusion process may be due to fractal flocs or clusters, rather than single particles. The gel may therefore appear as a space filling assembly of those flocs, suggesting that floc-floc interactions or mechanical connections may be crucial to determine not only the dynamics of the gel formation (Kroy et al. 2004; Del Gado et al. 2004) but also frozen-in stresses or gels mechanics. Existing studies of colloidal elasticity and rheology have mainly assumed completely rigid fractal flocs connected by weaker mechanical connections (Shih et al. 1990; Ramakrishnan et al. 2004), although this scenario may not be valid for a number of gels where the floc deformability, strong floc-floc interactions, and in general more complex mechanics may be at play.

This brief overview of different gelation scenarios, albeit limited to a simple suspension of colloidal particles, naturally highlights the diversity of structure, morphology, and mechanical characteristics of soft particulate gels. Gelation scenarios for biopolymers and other supramolecular polymer-based colloidal units are much more complex, with the build-up of the interconnected network being usually the last step of multiple hierarchical aggregation processes, leading to fibrils, micelles, or bundles (Tabatabai et al. 2015; Mao et al. 2016; Burla et al. 2020; Vereroudakis et al. 2020). In other cases, such as gels that are at the origin of cement cohesion and strength (Ioannidou et al. 2016), or that form during biomineralization (Shoaib et al. 2017), the development of the porous solid matrix takes place in presence of additional nonequilibrium processes and chemical reactions, more intricate sources of internal stresses, structural and mechanical heterogeneities, including the fact that the microscopic forces driving the aggregation may change over time. Understanding these more complex gels obviously requires a much more detailed insight into the hierarchical aggregation of the microstructure and lacks a theoretical framework for the microscopic forces and thermodynamic stability. However, we can still identify common traits with the simpler scenarios discussed above: gelation corresponds to the emergence of nonergodic states and it is associated to development of internal stresses, due to the geometric frustration in the aggregation of meso-scale gel constituents. These gel states and the microscopic stresses imprinted in the gel matrix depend on the gelation path, and there is a direct, albeit poorly understood, correspondence between the organization of the gel in space, the frozen-in stresses, and the gel mechanics.

To summarize, because soft particulate gels require a rigid matrix and the total solid volume fractions are typically quite low, structural heterogeneities tend to be large. Microscopic processes, more or less affected by the underlying thermodynamics, will favor different types of structural and morphological heterogeneities. In general, gelation will be associated to the build-up of frustration and local stress inhomogeneities over

different lengthscales. The outstanding questions are: is there an organizing principle in the gel microstructures that can encompass so many structures, processes and materials? Is it possible to develop a consistent fundamental understanding of their mechanics or identify common underlying mechanisms?

Origin of Elastic Modulus and Emergence of Rigidity

While the understanding of these phenomena is only nascent, there is growing evidence that 1) the mechanics of soft particulate gels are determined by mechanical heterogeneities and frozen-in stresses built-up during gelation, and 2) that the role of structural heterogeneities in the mechanical response and rheology is a hint to that. Figure 3 (right) revisits the equilibrium phase diagram for colloidal suspensions with short range attractive interactions (left, (b)) by complementing it with the hypothetical line along which the suspension could solidify into a gel, characterized by a finite low frequency elastic modulus G_0 that dominates its mechanical response (Zaccone et al. 2009). It is important to consider that the elastic response in the solid-like region (darkened) may be controlled by different lengthscales, as gelation conditions or solid volume fraction changes. In particular, the key lengthscale would grow from right to left, that is, going from the denser (and more structurally homogeneous) to the more dilute (and more structurally heterogeneous) gels. At sufficiently high volume fractions, these gels have solid matrices that are relatively homogeneous at the scale of the colloidal units, very similar to colloidal glasses. Even when considering the role of disorder, the elasticity of the material is largely set by the interactions between the colloidal units and the typical coordination number. As the colloidal gel assembly becomes more heterogeneous with decreasing the solid volume fraction, as discussed in the previous section, the elastic modulus of the gels can change by orders of magnitude even if the colloidal interactions are not significantly different. It is clear that the way the gel structure is spatially organized, rather than just the colloidal

interaction strength, plays a predominant role and in fact determines the elastic response.

Let's consider the case where initial steps of phase separation or irreversible aggregation among colloidal units lead to formation of clusters, but further growth or merging is kinetically arrested or geometrically frustrated. Hence, the gel appears as a dense assembly of such clusters (Ramakrishnan et al. 2004; Kroy et al. 2004; Del Gado et al. 2004; Laurati et al. 2009). Zaccone et al. (2009) proposed that in such microstructures the cluster-cluster interactions may dominate the elastic modulus. Using information from experiments on the attractive interactions between the colloidal units and on the cluster sizes, their simple theoretical framework allowed them to show that the elastic response is indeed dominated by the cluster-cluster connections and that the elastic modulus can be justified in those terms, once one makes the approximation of roughly spherical clusters, completely rigid, and joint by single particle connections. A recent study (Whitaker et al. 2019), combining microscopy, rheology, and numerical simulations with graph analysis, has shown that gels prepared by deep quenches in the spinodal region have such morphology, with clusters that are not necessarily spherical but are rather compact, relatively isotropic and likely rigid. Whitaker et al. (2019) have also demonstrated that, by systematically varying the colloidal interaction strength, the related change in the mechanical properties of the interparticle bonds does not account for the change in the modulus of the gel that can instead be explained only in terms of cluster-cluster connections. Further studies have identified the gelation in similar colloidal systems with a percolation of such clusters, potentially rigid, therefore also supporting the idea that cluster-cluster interactions dominate the elasticity of the gels (Tsurusawa et al. 2019).

Zaccone et al. (2009) also suggested that, with decreasing the solid content, as the structure of soft particulate gels becomes sparser and more open, the rigid units may be quite different from compact clusters, have to span larger lengthscales, and may be hard to separate out from the rest of the structure. If one could still identify the lengthscale that contributes most to the elastic

response, this would be larger in the sparser networks, and its relationship to the mesoscopic gel structure would be hard to disentangle.

Because of lower connectivity, nonaffine rearrangements are likely to be more pronounced and sensibly decrease the shear modulus of more dilute colloidal gels. Moreover, because removing even few colloidal units can significantly compromise the mechanical stability of these sparser networks, varying the solid content in this regime would have a stronger effect on the elastic modulus, as indeed suggested by the relatively strong dependences reported in very diluted colloidal gels (Shih et al. 1990; Gisler et al. 1999; Trappe et al. 2001; Del Gado et al. 2016). The role of larger scale connections across the gel structure also appears in the viscoelastic spectra, with the moduli varying over a wider range of frequencies and featuring extended power law regimes (Bremer et al. 1989; Curtis et al. 2013; Hung et al. 2015; Aime et al. 2018a; Keshavarz et al. 2021). These effects are often rationalized in terms of fractal microstructures, whose self-similarity is responsible to connect the particle-particle interaction strength to the overall modulus at very low solid content (Shih et al. 1990; Muthukumar 1989). However, such mechanical characteristics seem common to a wide range of soft particulate gels, in spite of the fact that the structural self-similarity does not always cover a range of length-scales sufficient to provide a robust justification. In fact, it seems that the low frequency elastic modulus and the shape of the viscoelastic spectrum are determined by both the connectivity and the topology of the gel microstructure (Bouziid et al. 2018), with the latter being much more difficult to characterize in these complex three-dimensional disordered and heterogeneous networks.

Some of these considerations point to the possibility that only a subpart of the gel microstructure is in fact responsible for the gel rigidity and hence for its elasticity, an idea reminiscent of the concept of the *elastically active chain* in polymer gels close to connectivity percolation (de Gennes 1979; Rubinstein and Colby 2003; Daoud and Coniglio 1981; Daoud 2000; Xing et al. 2004). For gels and soft amorphous solids in general, the

main theoretical framework to understand rigidity considers locally rigid structures, due to mechanical constraints such as chemical bonds or steric repulsion, that percolate through the material. The problem is hence translated into analyzing the onset of rigidity in a disordered network of springs, an abstraction of the actual solid, and its rigidity percolation (RP) transition (He and Thorpe 1985; Jacobs and Thorpe 1995). With respect to percolation phenomena controlled by the geometric connectivity (Sahimi 1998), the onset of rigidity requires a spanning cluster that is not just connected but also mechanically stable and able to transmit stresses. The condition for rigidity percolation is therefore typically achieved at higher solid volume fractions, with respect to connectivity percolation, whereas soft particulate gels can be mechanically rigid at volume fractions as low as a few percent (Trappe et al. 2001; Del Gado et al. 2016).

Starting from the fact that pronounced structural heterogeneities in colloidal gels are the manifestation of spatial correlations induced by colloidal interactions and specific gelation conditions (and can in fact be affected in different ways through the gelation process as discussed in section “[Source of Mechanical Heterogeneities and Frozen-in Stresses: Microscopic Forces and Gelation Processes](#)”), Zhang et al. (2019) have demonstrated that such spatial correlations can shift the RP to much lower volume fractions. Combining a lattice model and rigidity analysis, together with molecular dynamics simulations, Zhang et al. (2019) have shown that physical interactions and correlations naturally organize the colloidal units into thin structures that efficiently transmit stress, such as the Warren truss in $2d$, shown in Fig. 2 (center), which is a mechanical element well known in structural engineering and architecture for its ability to carry substantial load. Different gelation conditions can favor the growth of structures like the Warren truss in different amounts (see Fig. 2 center and right). However, the volume fraction of this one-dimensional structure in a two-dimensional plane vanishes in the thermodynamic limit, giving rise to rigidity at arbitrary low volume fractions. Recent experimental observations and simulations (Hsiao et al.

2012; Valadez-Pérez et al. 2013; Rocklin et al. 2021; Tsurusawa et al. 2019; Whitaker et al. 2019) support these findings, having highlighted the presence of locally rigid structures and their percolation in various colloidal gels.

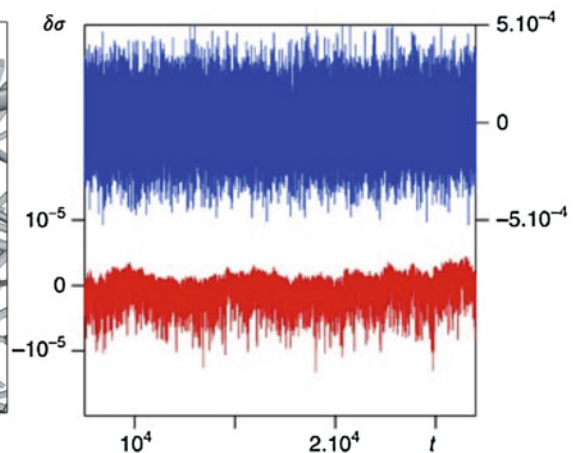
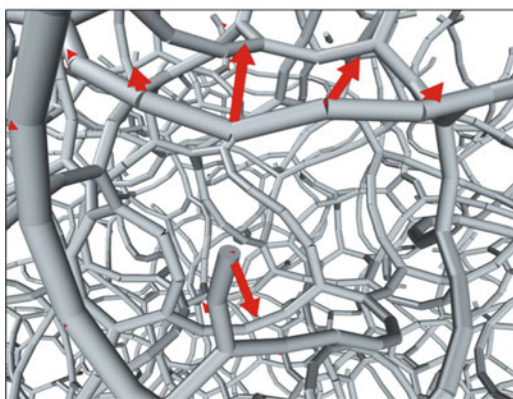
The idea that in soft particulate gels the gelation processes and the microscopic forces at play help select the smart structures needed for rigidity brings in a new perspective: the subpart of the gel microstructure actually determining its elastic response, may be related to localized stress patterns that naturally emerge during gelation and affect the linear and nonlinear mechanics of these materials. In particular, the development of locally rigid structures may naturally create (or contribute to) the mechanical heterogeneities previously discussed. It is worth considering that locally rigid structures may be formed at different times and through various processes, but the emergence of the gel rigidity through RP requires their spatial organization into a spanning rigid network, a nonlocal phenomenon. Hence, not all locally rigid structures identified at different steps may end up contributing in the same way to the gel rigidity and some of them may disappear in favor of others as the material solidifies. What are the implications of the development of smart rigid structures and of the role of rigidity percolation in the build-up of frozen-in stresses are among the outstanding questions.

Stress Localization at Rest and Under Shear

Frozen-in stresses in soft particle gels may be thought as elusive and negligible however they manifest even when the material is at rest. Depending on the size of the colloidal units and interaction strength, these solids can be more or less sensitive to thermal fluctuations, with spontaneous and thermally activated processes producing rich microscopic dynamics. Even at rest, thermal fluctuations can trigger ruptures of parts of the microscopic structure that are under tension or can promote coarsening and compaction of initially loosely packed domains, depending on the conditions under which the material initially

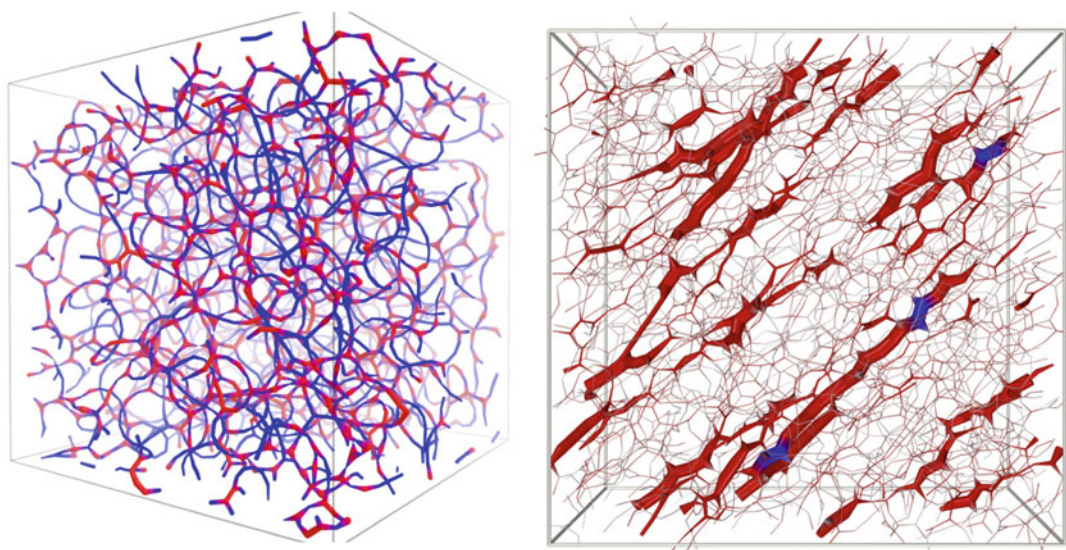
solidified: these processes underpin the aging of the microstructure and of the mechanical response of the gels. There is now extensive experimental evidence that the microscopic dynamics associated to these processes are intermittent and faster than exponential (Cipelletti et al. 2000; Ramos and Cipelletti 2001; Bellour et al. 2003; Bandyopadhyay et al. 2004; Maccarrone et al. 2010; Mansel and Williams 2015; Bandyopadhyay et al. 2004; Lieleg et al. 2011; Angelini et al. 2013; Ruta et al. 2014; Gao et al. 2015), suggesting an elastic rebound of the gel matrix as a response to microscopic restructuring (Bouchaud 2008; Ferrero et al. 2014). Bouzid et al. (2017) have proposed that the large stress heterogeneities frozen-in during solidification trigger microscopic rearrangements which are dominated by the elasticity stored in the material structure (Fig. 4). They have demonstrated that this elastically driven dynamics is intermittent and spatially correlated, markedly different from the spontaneous dynamics induced by thermal fluctuations close to equilibrium. Hence, the anomalous aging dynamics detected in experiments is the direct consequence of the internal stresses frozen-in during the gelation process and by the gel history.

Numerical simulations have access to local stresses in model gel networks and can provide direct insight into how locally competing stresses emerge during the gelation process and in different processing conditions (Fig. 5, left) (Colombo and Del Gado 2014b; Bouzid et al. 2017; Johnson and Zia 2021), an information that cannot be easily accessed by experiments. Building on this capability, and in feedback with experiments, computational studies can help develop the link between the stresses localized in the gel structure and its mechanical response (Bouzid and Del Gado 2020). Under deformation, localized stresses naturally become sources of nonaffine motion and, together with the disorder of the gel structure, favor further stress localization (Colombo and Del Gado 2014b): the sparsely connected structure of soft particulate gels helps concentrate stresses and the stress localization can initiate, at large deformation, large scale damage of the structure itself. Recent studies have demonstrated that just the network topology can control the nonlinear behavior of gel networks, beyond the properties of the single components (fiber, particles, or agglomerates), and can determine, alone, the softening or stiffening nature of the gel response (Bouzid and Del Gado 2018). Recent explorations of the link between disorder/



Stress Localization in Soft Particulate Gels, Fig. 4 Elastically driven intermittent dynamics. Left: sketch of break-up of gel connections during aging, due to frozen-in stresses. Right: stress fluctuations become intermittent and strongly correlated when elasticity

dominates the microscopic rearrangements. (Reproduced from Bouzid et al. (2017) with permission. Creative Commons license available at <https://creativecommons.org/licenses/by/4.0/>.)



Stress Localization in Soft Particulate Gels, Fig. 5 Stress localization in soft particulate gels. Left: Gelation results in frozen-in stresses in a model gel network, with parts of the structure preferentially contribute to tension (blue) or compression (red). (Reproduced from (Bouzid et al. 2017) with permission). Right: Tensions localize in a small portion of the overall network under

shear, in a model gel network. The visualization from numerical simulations depicts as thicker the regions where tension is higher. (Reproduced from (Colombo and Del Gado 2014b) with permission. Creative Commons license available at <https://creativecommons.org/licenses/by/4.0/>.)

connectivity/failure in collagen gels (Burla et al. 2020), central to biological tissues, and of microscopic precursors in the failure of colloidal materials (de Oliveira Reis et al 2019; van Doorn et al. 2018; Aime et al. 2018b) point in the same direction. The spatial organization of the gel matrix and the microscopic forces that helped make it mechanically stable hold crucial information on the gel nonlinear response and failure, because they determine the initial stress localization pattern and its evolution under external load. Deeper understanding of how localized stress patterns emerge in soft particulate gels and how they evolve as the material is processed or used is therefore the key to new theories and constitutive models and the various questions outlined in this chapter.

Future Directions

Circling back to the initial discussion, the variety and complexity of microstructures and the

nonequilibrium nature of soft particulate gels make it difficult to identify organizing principles and fundamental mechanisms, but the common trait of localized stress patterns emerging from mechanical constraints and the fact that they control the evolution and the response of these materials indicate a path for future research directions.

A systematic characterization of the consequences of specific stress states and patterns built through various gelation processes or across different gels would provide deeper insight into the role of frozen-in stresses and their consequences for the mechanical response. Understanding the emergence of rigidity can provide a different perspective, complementary to the thermodynamics of the colloidal solutions or the models for colloidal aggregation, needed to capture structure formation and development of frozen-in stresses in soft particulate gels. It will connect the physics of these very soft materials to the one of granular matter and of other amorphous solids, where mechanical constraints and localized stress pattern are key.

Complementing experiments with numerical simulations and connecting to theoretical approaches for rigidity percolation and topological mechanics will be essential to go from microscopic processes and material specificity to critical lengthscales, geometry and implications of localized stress patterns for the mechanical response.

The question of how mechanical constraints and localized stresses evolve in time, under load, and with varying deformation, is at the core of understanding how frozen-in, localized stresses can help promote or prevent instabilities when driving a soft gel toward yielding, jamming, or hardening. In particular, identifying microscopic precursors to failure and yielding, understanding their possible connections to specific frozen-in stresses, and their time evolution, is central to gain insight into the complex nature of failure or yielding in these very soft materials and into toughening, embrittlement, or self-healing of gel structures.

Investigating along these lines will certainly require combining different approaches, analytical theories with numerical simulations and multiple experimental techniques, crossing boundaries across traditionally distinct areas in material physics, bridging fundamental and applied research.

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Nonlinear Mechanics of Colloidal Gels: Creep, Fatigue, and Shear-Induced Yielding

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Article Outline

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Glossary

Colloids Refers to entities, such as particles or polymers, smaller than a few microns in size and sensitive to thermal agitation. Colloids therefore display Brownian motion when dispersed at low volume fraction in a solvent. They encompass a broad range of entities from proteins and clay particles to synthetic polymeric particles and come in all sorts of geometrical shapes, such as spheres, platelets, and rods. Colloids are also subject to a wide variety of interactions, which gives rise to rich state diagrams including fluid and crystalline equilibrium phases as well as out-of-equilibrium states such as gels and glasses.

Colloidal gels Refers to soft solids, whose structure is composed of attractive colloids that form a space-spanning network. Colloidal gels are in an out-of-equilibrium state and display mainly solid-like properties at rest and under mild deformations, i.e., their elastic modulus is much larger than their viscous modulus in the linear regime. Upon increasing external mechanical constraints, their viscoelastic response becomes nonlinear and generally involves a yield point above which colloidal gels show liquid-like properties (see “Yielding” below).

Creep Refers to the motion induced by imposing a constant load to a material, whose response is quantified by the resulting deformation or strain.

Fatigue Refers to the phenomena induced by imposing an oscillatory load of constant amplitude to a material, whose response is quantified via the temporal evolution of its viscoelastic properties.

Yielding Refers to a solid-to-liquid transition induced by imposing some deformation or stress to a material. The yield stress and yield strain are respectively the critical stress and strain above which a complex material starts to flow or loses its integrity. The yielding transition often involves a complex spatio-temporal scenario, which is still the topic of intense research effort.

Definition of the Subject

Colloidal gels are formed through the aggregation of attractive particles, whose size ranges from 10 nm to a few micrometers, suspended in a liquid. Such gels are ubiquitous in everyday life applications, from food products to paints or construction materials, in particular thanks to their ability to easily “yield,” i.e., to turn from a solid to a liquid under the application of a weak external load. Understanding and controlling the mechanical response of colloidal gels is, therefore, of prime importance. Depending on the details of

the system, however, the resulting gel networks present different microstructural organizations that may lead to widely different mechanical responses. This raises important challenges in fully characterizing yielding and in uncovering the mechanisms of nonlinear response in colloidal gels. In this entry, we distinguish between two classes of colloidal gels showing respectively reversible yielding, where the gel network reforms upon load release, and irreversible yielding, where the network is fully destroyed through fractures and phase separation. This broad, empirical distinction is achieved through rheology and local experiments at a mesoscopic scale, intermediate between the network characteristic size and the sample size. We further discuss how the observables derived from creep and fatigue experiments may be modeled to predict yielding and highlight open questions and future research directions in the domain.

Introduction: From Gelation to Rupture in Colloidal Dispersions

General Context: The Mechanics of Colloidal Gels

In mechanics, material rupture refers to a catastrophic series of microscopic events that lead to the macroscopic, irreversible failure of a material under an applied load. Studying the onset of rupture and rupture itself is crucial in fields like earthquake studies and construction materials where understanding and being able to predict the rupture of hard materials is at the core of people's safety (Sornette 2002; Alava et al. 2006; Dixon et al. 2014). In soft solids such as gels, rupture is less dramatic but just as important.

A colloidal gel forms whenever attractive colloidal particles dispersed in a fluid aggregate into a loose, fragile network that percolates across the sample volume (Larson 1999; Mewis and Wagner 2012). Colloidal gels are found in a huge number of practical situations, from pharmaceutical and food products (Gibaud et al. 2012; Mezzenga and Fischer 2013) to construction materials like cement (Lootens et al. 2004; Ioannidou et al. 2016), as well as ink-jet printing (Lewis 2002;

Smay et al. 2002; Tan et al. 2018) or flow-cell batteries (Youssry et al. 2013; Fan et al. 2014; Helal et al. 2016; Narayanan et al. 2017). Such ubiquity results from the peculiar mechanical response of colloidal gels: while they behave like soft elastic solids at rest, with an elastic modulus in the range of 1 Pa–10 kPa, colloidal gels are easily made to flow upon application of mild external stresses including shear, compression, gravity or vibration. This solid-to-liquid out-of-equilibrium transition is referred to as the “yielding transition,” and a fundamental understanding of the various steps involved in such a transition is of prime importance for applications to material design and industrial processes (Balmforth et al. 2014; Bonn et al. 2017). For instance, in food science, the texture and yielding properties of edible gels control mouth feel (Jetlema et al. 2016; Wagner et al. 2017) but is also at the heart of food design for people with swallowing problems such as toddlers or elderly people (Aguilera and Park 2016).

Depending on the nature of the particles and due to the wide variety of ways to induce gelation, e.g., through electrostatic interactions, dipole-dipole interactions, pH, or temperature variations, gel networks present a broad variety of structural organizations at the microscopic scale (Nicolai and Durand 2013; Mezzenga and Fischer 2013). The mechanical properties of colloidal gels are then encoded in the colloidal interactions and the gel structure.

In particular, the gel structure is expected to have a significant impact on the way the gel fails under stress. Yet, uncovering the exact link between the interparticle potential, the gel structure, and the gel mechanical properties is tricky and currently constitutes an active research domain. Such a difficulty can be mainly attributed to the fact that colloidal gels are out-of-equilibrium phases with a complex microstructure that is itself pushed into a nonlinear regime due to the applied stress. Rationalizing the link between the gel structure and the failure scenario, therefore, remains a complex exercise that we shall approach here by considering two limiting cases, both in the gel structure and in the rupture mechanisms. Indeed, the main goal of this paper is to apprehend the various yielding processes in

colloidal gels through two systems with similar elasticity at rest and yet very distinct rupture mechanisms: a carbon black gel that shows *reversible* fluidization upon yielding (also commonly referred to as shear-rejuvenation) and a sodium caseinate gel that displays *irreversible* brittle failure akin to hard solids (also referred to as brittle-like failure).

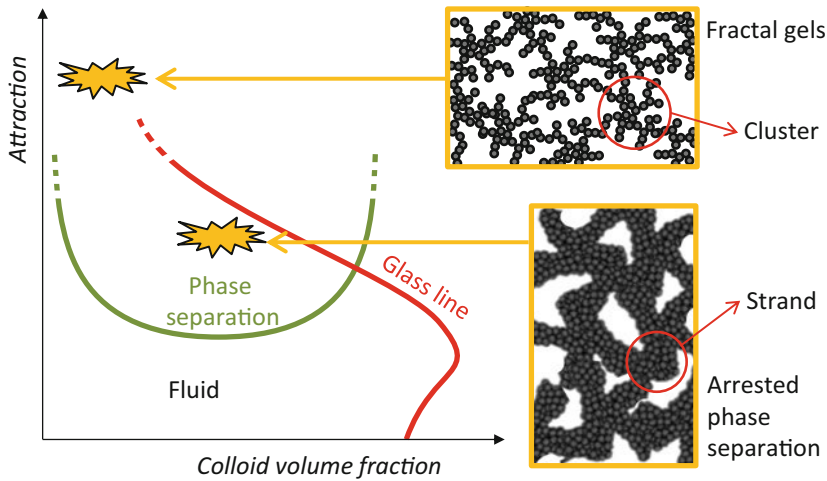
In the rest of this section, we first briefly remind the reader about the most common gelation pathways in attractive colloids and describe the two gel systems that we will use to illustrate our discussion on yielding processes. We then introduce the rheological measurements that are usually performed to assess the nonlinear mechanical response of colloidal gels. In section “[Reversible Yielding Versus Irreversible Rupture](#),” we distinguish experimentally between two types of yielding behaviors in colloidal gels, namely reversible vs. irreversible yielding, both from a macroscopic point of view and from local approaches. Finally, section “[Fundamental Questions and Perspectives](#)” further generalizes the previous observations based on the current literature and highlights open questions in the domain.

A Brief Reminder on Colloidal Gelation

As sketched in Fig. 1, two limit scenarios can be distinguished in the case of colloids with short-range attraction (Trappe and Sandkühler 2004; Zaccarelli 2007). In the extreme case of very strong interparticle attraction and very low volume fractions, the regime of so-called “irreversible aggregation” is reached, and one observes the formation of soft fractal gels (Shih et al. 1990; Krall and Weitz 1998). In this regime, the intermediate entities between the particle size and the gel network are fractal clusters, i.e., fractal aggregates of individual colloids. The particles within the clusters are trapped in the potential well of their neighbors so that their motion is constrained, thereby leading to arrested dynamics and providing elasticity to the network. At intermediate attraction strength and concentrations, the regime of so-called “arrested phase separation” is reached (Foffi et al. 2005; Cardinaux et al. 2007; Buzzaccaro et al. 2007; Lu et al. 2008). In this regime, a gel results from the interplay between

phase separation and the glass transition line: the dispersion is unstable and phase separates into a bi-continuous network (spinodal structure) composed of a “gas” phase, i.e., a dilute phase of colloids, and a “liquid” phase, i.e., a dense phase of colloids. During the phase separation process, the concentration of the liquid phase increases and eventually meets the glass line where the liquid network becomes glassy, thus “freezing” the process of phase separation. Such arrested dynamics leads to a long-lived network of particles with a spinodal structure (Gibaud and Schurtenberger 2009; Gibaud et al. 2012; Gao et al. 2015; Da Vela et al. 2016). Here, the intermediate entities between the particle size and the gel network are the network strands. Strands are composed of densely packed attractive particles and provide rigidity to the network.

Although very simplified, Fig. 1 illustrates how the gelation kinetic pathway may affect the microstructure of the resulting colloidal gel. Since the microstructure directly impacts the mechanical properties of these out-of-equilibrium systems, controlling the route to gelation offers a way to tune gel properties. A common way to control gelation consists in using particles with an interaction potential that is sensitive to an external stimulus such as pH or temperature (Gosal and Ross-Murphy 2000). By increasing the attraction strength, one can continuously go from a fluid state to a gel state. Another common way to control the gel state consists in playing with the shear history experienced by the system during or after gelation (Ovarlez et al. 2013; Koumakis et al. 2015; Helal et al. 2016; Narayanan et al. 2017; Hipp et al. 2019; Jamali et al. 2020). By tuning the way a colloidal gel is sheared or mixed, one may vary its terminal structure and mechanical strength without changing the interparticle potential. Two experimental knobs may be controlled: the preshear intensity and the rate of flow cessation. On the one hand, gels reformed after strong shearing and “instantaneous” flow cessation generally evolve into stronger solids with a relatively homogeneous and fine microstructure, whereas the application of weak shear rates leads to weaker gels with a coarser microstructure (Koumakis et al. 2015). On the other hand, a preshear of



Nonlinear Mechanics of Colloidal Gels: Creep, Fatigue, and Shear-Induced Yielding, Fig. 1 Schematic state diagram for colloidal particles with short-range attraction. In the extreme case of very strong interparticle attraction and very low volume fractions, colloids aggregate into fractal gels, whereas at intermediate strength of attraction

and volume fractions, gels result from the interplay between phase separation (the green line indicates the binodal line) and the glass transition (red line). Those two types of gels have very different structures, characterized by clusters for fractal gels and network strands for arrested phase separation gels

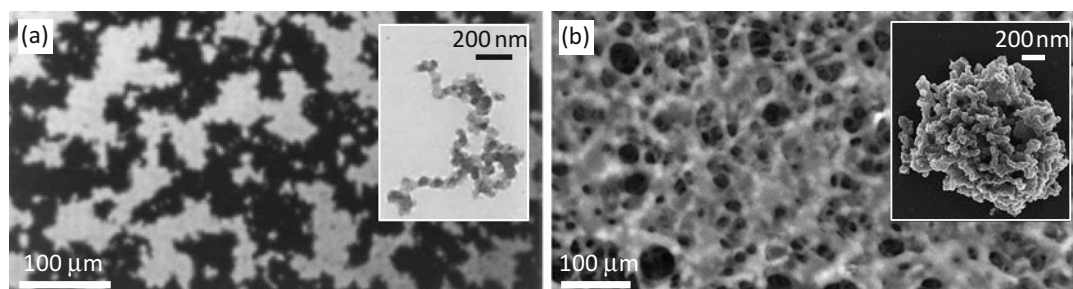
large intensity followed by flow-cessation experiments performed at different rates allows one to tune continuously the gel microstructure. For instance, it was shown for some fractal gels that the slower the flow cessation, the less connected and the weaker the resulting gel (Helal et al. 2016). A major difference in the final gel states accessed via continuous quenching of pH or temperature and mechanical shearing lies in the anisotropy and residual stresses associated with the latter (Grenard et al. 2014; Colombo et al. 2017; Sung et al. 2018).

Two Illustrations of Colloidal Gel Microstructures

To apprehend the mechanical properties of colloidal gels, we focus on two systems with distinct gelation pathways and microstructures: (i) a dispersion of carbon black particles in oil (Trappe and Weitz 2000) and (ii) an acid-induced sodium caseinate gel (Bremer et al. 1990; Braga et al. 2006).

Carbon black gels are composed of carbon black particles dispersed in oil and are a reasonable realization of fractal gels that result from cluster aggregation (Donnet et al. 1993; Trappe and Weitz 2000). Carbon black particles are

obtained from partial combustion of fuel and are made of unbreakable aggregates of permanently fused nanometric primary particles. These aggregates have a typical diameter of 500 nm. When dispersed in a light mineral oil at a weight concentration of a few percent, carbon black particles form a space-spanning gel network of fractal dimension $d_f \simeq 2.2$ due to attractive Van der Waals interactions of typical strength $U \sim 30 k_B T$ (Hartley and Parfitt 1985; Trappe et al. 2007; Richards et al. 2017). Representative pictures of the carbon black gel microstructure and an individual carbon black particle are shown in Fig. 2a. The initial gel state is obtained by preshearing the suspension at $+1000 \text{ s}^{-1}$ then at -1000 s^{-1} for 20 s each, in order to break up any large aggregates. Abrupt flow cessation quickly leads to the gel formation (in less than a second), which is then left at rest for 100 s before performing any subsequent test. All results concerning carbon black gels presented in this article are based on such a preshear protocol. Note that preshear not only rejuvenates the sample by erasing its previous shear history, it also selects a specific reproducible microstructure with some degree of anisotropy and stored internal stresses that may play a significant role in the subsequent mechanical response



Nonlinear Mechanics of Colloidal Gels: Creep, Fatigue, and Shear-Induced Yielding, Fig. 2 Microstructures of two colloidal gels. (a) Optical microscopy image of a carbon black dispersion at 0.064 vol % in light mineral oil. (Adapted from Trappe and Weitz (2000) with permission from the American Physical Society.) Inset: transmission electron microscopy image of an individual carbon black

particle. (Adapted from Ehrburger-Dolle et al. (1990) with permission from Elsevier.) (b) SEM microscopy image of a sodium caseinate gel at 4 wt % in water acidified with 1 wt % GDL (unpublished data). Inset: SEM image of an individual sodium caseinate particle at pH = 3.5. (Adapted from Coskun et al. (2015) with permission from Elsevier)

(Osuji et al. 2008; Negi and Osuji 2009; Grenard et al. 2014; Helal et al. 2016).

Sodium caseinate gels are made of sodium caseinate proteins dispersed in water and can be seen as a close realization of arrested phase separation. Sodium caseinate is a by-product of casein, which is the main protein component of milk (Fox 2003). Casein is present in the form of polydisperse spherical complexes containing casein proteins and colloidal calcium phosphate. Four main casein proteins may be distinguished, namely α_1 -, α_2 -, β -, and κ -casein, with typical weight ratios 0.4:0.08:0.4:0.1 and approximately the same molar mass $M \simeq 2 \cdot 10^4 \text{ g} \cdot \text{mol}^{-1}$ (HadjSadok et al. 2008). The native casein complex dissociates after removal of the colloidal calcium phosphate, yielding a mixture of individual casein proteins referred to as sodium caseinate with an average diameter of 400 nm (Coskun et al. 2015). Sodium caseinate particles display a mixed interparticle potential: a short-range attraction and a long-range electrostatic repulsion due to the protein surface charges. Gelation can be obtained by turning down the electrostatic repulsion. This can be achieved using the pH as a control parameter thanks to the presence of carboxylate and primary amine groups at the surface of the sodium caseinate, which charge depends on the pH. At pH = 7, sodium caseinates are on average positively charged, and an aqueous dispersion of caseinate is stable and translucent. All sodium caseinate gels discussed here are obtained

by using glucono- δ -lactone (GDL), a molecule that slowly hydrolyzes into gluconic acid and thus continuously, and homogeneously lowers the pH of the sodium caseinate dispersion from 7 to 3. This GDL-controlled acidification enables the formation of a bulk gel phase around the isoelectric point – the point where surface charges vanish on average – at $\text{pH}_{\text{cas}} = 4.6$. At pH = pH_{cas} , the gelation is kinetically driven by diffusion-limited cluster aggregation (DLCA) (Bremer et al. 1990). Right below pH_{cas} , at pH = 3, sodium caseinates have slightly negative surface charges and over-acidification results in the coexistence of a “gas” phase of dilute sodium caseinates and a glassy network (Leocmach et al. 2015), a scenario that is consistent with arrested phase separation (Cardinaux et al. 2007). Figure 2b displays an example of scanning electron microscopy (SEM) image of an acid-induced sodium caseinate gel together with an SEM image (as an inset) of an individual sodium caseinate particle at pH = 3.5. The gel structure is made of strands with a typical width of 1 μm . All mechanical characterizations presented below are performed on sodium caseinate gels prepared in situ, i.e., for which acidification is performed directly in the measurement cell.

A First Approach of Yielding Based on Oscillatory Shear Rheometry

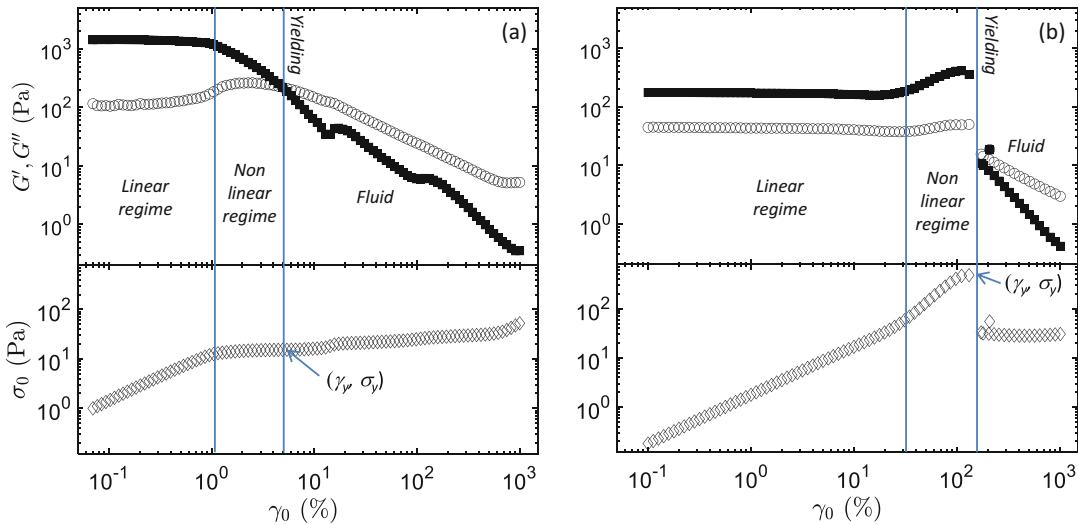
The two colloidal gels presented above result from very different gelation pathways and thus present very different microstructures. The main

question that we wish to address in the following is: how do their nonlinear mechanical responses differ? As a first approach of this question, we now introduce the widespread toolbox of rheology to induce and assess gel yielding.

The mechanical response of soft materials is most commonly probed through shear rheometry, where the sample is confined between a fixed boundary and a rotating tool and the shear stress σ and strain γ are measured at a macroscopic level, respectively through the torque applied on the rotating tool and its displacement (Macosko 1994). One usually explores the gel mechanical behavior from the linear elastic regime up to failure thanks to oscillatory shear. More specifically, in a strain-sweep experiment, the rheometer imposes an oscillatory strain $\gamma(t) = \gamma_0 \cos(2\pi ft)$ of increasing amplitude γ_0 at a frequency f , and records the corresponding stress response $\sigma(t)$. Linear response theory allows one to define the response function G^* that relates the stress to the strain as $\sigma = G^* \gamma$ in complex notation. G^* is referred to as the complex modulus of the gel and can be decomposed into its real part, the elastic (or storage) modulus G' that indicates how much elastic energy the gel can store, and

its imaginary part, the viscous (or loss) modulus G'' that indicates how much energy is lost due to dissipation.

Figure 3 compares the mechanical properties G' and G'' of a carbon black gel (Fig. 3a) and those of a sodium caseinate gel (Fig. 3b) as a function of the strain amplitude γ_0 . For both systems, the gel response to oscillatory shear can be decomposed into three different regimes depending on γ_0 . At small γ_0 , in the linear viscoelastic regime, the stress amplitude σ_0 is simply proportional to the strain amplitude γ_0 : the sample mechanical properties are entirely characterized by the elastic modulus G' and loss modulus G'' . For the gels under study, G' is of the order of 100–1000 Pa and much greater than G'' , a characteristic of soft solids. Upon increasing γ_0 , the strain response becomes non-linear. Therefore, linear response theory no longer strictly applies, and G' and G'' only provide information on the material response at the fundamental frequency f . In other words, higher harmonics of the stress $\sigma(t)$ must be taken into account to fully characterize nonlinear viscoelasticity (Hyun et al. 2011). Eventually, above a critical strain γ_y defined as the strain where $G' = G''$, the gel yields and subsequently flows



Nonlinear Mechanics of Colloidal Gels: Creep, Fatigue, and Shear-Induced Yielding, Fig. 3 Assessing yielding from oscillatory shear. Elastic modulus G' (■), viscous modulus G'' (○) and stress amplitude σ_0 (◇) as a function of the amplitude γ_0 of oscillatory strain at frequency

$f = 1$ Hz in (a) a carbon black dispersion at 6 wt % in light mineral oil (adapted from Perge et al. (2014) with permission from the Society of Rheology) and (b) a sodium caseinate gel at 4 wt % in water acidified with 4 wt % GDL (unpublished data)

like a liquid: this critical strain γ_y corresponds to the *yield strain* that can be inferred from large-amplitude oscillatory shear (LAOS) and the corresponding stress is associated with the *yield stress* σ_y . Note that such definitions of the yield strain and stress are obviously protocol-dependent (Bonn et al. 2017) and that in the case of the carbon black gel, G' displays two local maxima beyond the yield point, which have been interpreted respectively in terms of inter-cluster and intra-cluster bond-breaking (Koumakis and Petekidis 2011).

While being qualitatively similar, the behaviors of G' and G'' as a function of the strain amplitude hint at different mechanical scenarios for the two gels under study even long before yielding. One may first note that although its elastic modulus at rest is about 10 times larger than that of the sodium caseinate gel, the carbon black gel enters the nonlinear regime and then yields at strain amplitudes that are about 10 times smaller than in the sodium caseinate gel. Thus, the more elastic, fractal gel constituted of particle clusters is more sensitive to external strain than the softer yet more “resistant” gel, whose structure is made of strands. Second, in the “medium-amplitude oscillatory shear” (MAOS) regime, the carbon black gel shows *strain softening*, i.e., the elastic modulus drops for $\gamma_0 \gtrsim 1\%$ and the stress amplitude σ_0 plateaus as a function of γ_0 , while the sodium caseinate gel displays *strain stiffening*, i.e., G' increases for $\gamma_0 \gtrsim 20\%$ and σ_0 increases faster than linearly with γ_0 . Third, contrary to the carbon black gel that shows a smooth, continuous variation of the various observables at the yielding transition, the sodium caseinate gel displays a strong discontinuity. In particular, the stress abruptly drops at yielding, which is indicative of the sample fracture. Indeed, visual inspection on the sample in a concentric-cylinder geometry reveals that the sodium caseinate gel fractures irreversibly at yielding, as also described in more details in section “Characterizing Yielding Through Spatially-Resolved Dynamical Measurements.”

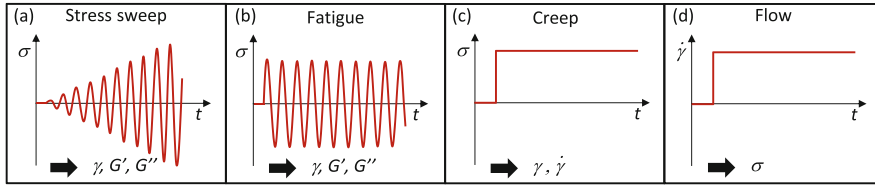
To summarize, the above description of strain sweeps remains only qualitative and does not provide full details on the yielding scenario.

Although the rheological response allows estimating the yield stress σ_y and the yield strain γ_y of the gel, it is insufficient to characterize the gel yielding as it does not provide any time-resolved information. This calls for more refined, time-resolved measurements, both macroscopic and microscopic, to uncover the reasons for the specific variations of G' and G'' exemplified in Fig. 3.

Reversible Yielding Versus Irreversible Rupture

In this section, we offer a time-resolved analysis of the yielding transition of colloidal gels at the macroscopic level. Indeed, the amplitude sweep protocol used so far to characterize yielding and sketched in Fig. 4a does not allow one to disentangle the effects of increasing the stress or strain from the temporal evolution of the sample, e.g., due to slow damage accumulation. In fact, there is a major difference between the yielding behaviors of the two systems presented above. Whilst the carbon black gel swiftly reforms and regains elasticity once the external load is released, i.e., yielding and shear-induced fluidization are to some extent *reversible*, the sodium caseinate gel remains liquid-like beyond the yield point, and composed of macroscopic pieces of the original gel network that coexist with the “gas” phase of dilute sodium caseinates. The protein gel is permanently broken and the yielding process thus appears as *irreversible*. In amplitude sweep experiments, such a striking difference only shows through the discontinuity reported in Fig. 2b and through the fact that one may perform several successive identical sweep tests on the carbon black gels, leading to reproducible results (provided that two consecutive tests are separated by the same preshear step), whereas one needs to prepare a fresh protein gel prior to each experiment.

To better characterize the two types of yielding scenarios and quantify their dynamics, we consider other mechanical tests, namely fatigue and creep tests that are schematized respectively in Fig. 4b and c. Contrary to stress sweep experiments, the input signal is stationary, which



Nonlinear Mechanics of Colloidal Gels: Creep, Fatigue, and Shear-Induced Yielding, Fig. 4 Rheological tests used to probe yielding in colloidal gels. (a) Stress amplitude sweep at fixed frequency. (b) Fatigue test under an oscillatory shear stress of constant amplitude and frequency. (c) Creep test under a constant shear stress. (d) Shear start up test under constant imposed shear rate. The

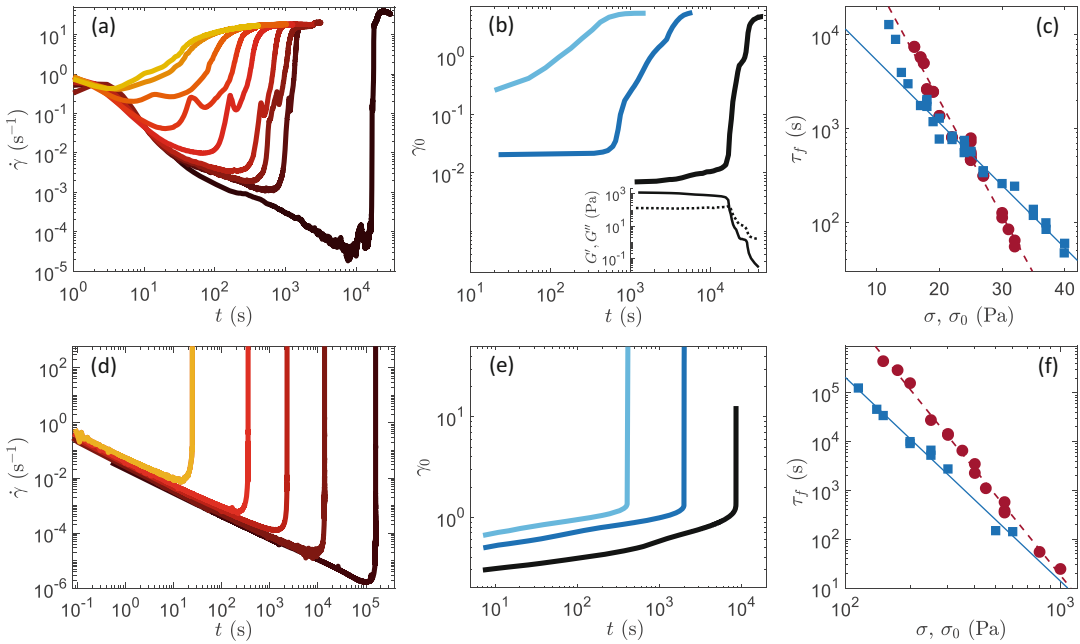
imposed variable in (a)–(c) is the stress σ . The measured observables are the strain γ , the elastic modulus G' and the viscous modulus G'' in (a, b) and the strain γ in (c) or equivalently its time-derivative, the shear rate $\dot{\gamma}$. In (d), the imposed variable is the shear rate $\dot{\gamma}$ and the measured variable is the stress σ .

facilitates the analysis of the material response and its time dependence. The primary objective of those tests is to determine the fluidization (or fracture) time τ_f defined as the time needed for the gel to become fluid as a function of the input parameter. Stress-controlled experiments such as fatigue or creep tests provide a relationship τ_f vs. σ , which characterizes the yielding dynamics at the macroscopic scale. We will show that the functional form of $\tau_f(\sigma)$ is representative of the rupture mechanism and allows one to differentiate between reversible and irreversible yielding. We will then briefly turn to local measurements that provide additional insight into the yielding process at the “mesoscale,” i.e., at spatial scales intermediate between the macroscopic scale probed by rheometry and the microscopic scale of the colloidal gel network.

Carbon Black Gels as Model Materials for “Reversible” Yielding

The yielding dynamics of carbon black gels associated with creep tests and fatigue tests is presented in Fig. 5a–c. In both cases, the yielding transition is strongly time- and load-dependent. Figure 5a shows the evolution of the shear rate $\dot{\gamma}$ as function of time t under constant stress amplitudes σ (increasing from right to left). All measurements show similar features: $\dot{\gamma}$ first slowly decreases at short times, then shows an abrupt increase and presents one or several kinks and fluctuations before a final increase up to a steady state. The whole process takes from a few seconds for large stresses to several hours at low stresses.

The fluidization time τ_f is defined as the inflection point during the final increase of $\dot{\gamma}$. Measurements of the velocity field within the gel revealed that the inflection point indeed corresponds to the point where the sample flows homogeneously like a liquid (Gibaud et al. 2010; Grenard et al. 2014). Similarly, Fig. 5b displays the temporal evolution of the strain amplitude γ_0 in response to three different fatigue tests (i.e., oscillatory shear stress at constant stress amplitude) conducted at various amplitudes σ_0 . Here again, all measurements show the same trend: a slow initial increase of γ_0 followed by a final increase up to a steady state. As shown in the inset of Fig. 5b, the final increase of γ_0 corresponds to the transition from a solid-like state where $G' > G''$ to a fluid-like state where $G'' > G'$. The fluidization time τ_f is here defined as the inflection point of the final increase of γ_0 , which corresponds to the time where the two moduli roughly coincide, $G' \simeq G''$, at least for low enough stress amplitudes (see inset in Fig. 5b). The time-dependence observed here is usually referred to as “delayed flow” or “delayed yielding” in the literature (Gopalakrishnan and Zukoski 2007; Sprakel et al. 2011; Lindström et al. 2012). Finally, note that in both creep and fatigue tests, a steady state is reached where the carbon black dispersion flows like a liquid. When the test is stopped and the stress is released, the dispersion aggregates again into a gel. As a result, successive yielding experiments can be performed on a single sample provided that the same pre-shear protocol is repeated between each test to prepare the sample into the same initial state.



Nonlinear Mechanics of Colloidal Gels: Creep, Fatigue, and Shear-Induced Yielding, Fig. 5 Comparison between creep and fatigue experiments in carbon black gels and sodium caseinate gels. (a)–(c) Delayed yielding in carbon black gels. (a) Creep experiments in a carbon black gel at 8 wt % in light mineral oil: shear rate responses $\dot{\gamma}(t)$ for different shear stresses σ applied at time $t = 0$ ($\sigma = 45, 50, 52, 53, 55, 60, 65, 70$, and 75 Pa from right to left, adapted from Grenard et al. (2014) with permission from the Royal Society of Chemistry). (b) Fatigue experiments in a carbon black gel at 6 wt % in light mineral oil: strain amplitude response $\gamma_0(t)$ to oscillatory stresses of frequency $f = 1$ Hz and amplitude $\sigma_0 = 11, 15$ and 27 Pa from right to left. Inset: G' (solid line) and G'' (dashed line) as a function of time t for $\sigma = 11$ Pa. (Adapted from Perge et al. (2014) with permission from the Society of Rheology and Gibaud et al. (2016) with permission from the Royal Society of Chemistry). (c) Fluidization time τ_f as a function of stress σ in creep experiments ($\bullet$) and as a function of stress amplitude σ_0 in fatigue experiments ($\blacksquare$) for a carbon black gel at 6 wt % in light mineral oil. Lines corresponds to the best exponential fits of the data: $\tau_f \sim \exp(-\sigma/\sigma^*)$ with $\sigma^* = 7$ Pa

for fatigue and $\sigma^* = 3.5$ Pa for creep experiments. (Adapted from Grenard et al. (2014) and Gibaud et al. (2016) with permission from the Royal Society of Chemistry.) (d–f) Brittle fracture in sodium caseinate gels. (d) Creep experiments in an aqueous gel of sodium caseinate at 4 wt % acidified with 1 wt % GDL: shear rate responses $\dot{\gamma}(t)$ for different shear stresses σ applied at time $t = 0$ ($\sigma = 200, 300, 400, 550$, and 1000 Pa from right to left, adapted from Leocmach et al. (2014) with permission from the American Physical Society). (e) Fatigue experiments in an aqueous gel of sodium caseinate at 6 wt % acidified with 6 wt % GDL: strain amplitude response $\gamma_0(t)$ to oscillatory stresses of frequency $f = 1$ Hz and amplitude $\sigma_0 = 90, 150$ and 200 Pa from right to left. (Adapted from Saint-Michel et al. (2017) with permission from the Royal Society of Chemistry.) (f) Fluidization time τ_f as a function of stress σ in creep experiments ($\bullet$) and as a function of stress amplitude σ_0 in fatigue experiments ($\blacksquare$) for a sodium caseinate gel at 4 wt % in water acidified with 1 wt % GDL. Lines correspond to the best power-law fits of the data: $\tau_f \sim \sigma^{-\beta}$ with $\beta = 4.2$ for fatigue and $\beta = 5.5$ for creep experiments (unpublished data)

Based on series of creep and fatigue tests, one may then access the dependence of τ_f with the applied stress. As shown in Fig. 5c, such a dependence is well captured by an exponential decrease, $\tau_f = \tau_0 \exp(-\sigma/\sigma^*)$, for both types of tests, although with different characteristic stresses σ^* and prefactors τ_0 . Such an empiric law was first reported for carbon black gels in (Gibaud et al.

2010; Sprakel et al. 2011). It is well captured by a mean-field model based on Kramers' theory for activated processes (Sprakel et al. 2011; Lindström et al. 2012; Gibaud et al. 2016). In this framework, yielding results from the competition between individual interparticle bond formation and rupture events induced by the external stress. Moreover, the characteristic stress σ^*

reflects the mean elastic barrier that should be overcome for a single bond to break. Typical values of σ^* in carbon black gels range from 1 to 10 Pa. We note from Fig. 5c that this stress barrier is smaller in creep experiments than in fatigue experiments ($\sigma^* \simeq 3.5$ Pa vs. $\sigma^* \simeq 7$ Pa resp.). Such an Arrhenius-like behavior of τ_f is observed in many other types of colloidal gels that also show reversible yielding, including depletion gels (Ramakrishnan et al. 2005; Dibble et al. 2006; Koumakis et al. 2015; Sprakel et al. 2011), presheared proteins gels (Brenner et al. 2013), and thermo-reversible gels (Gopalakrishnan and Zukoski 2007). As for carbon black gels, they appear as a model system to investigate delayed yielding. For the sake of simplicity, we only focus here on τ_f . Yet, we emphasize that the fluidization process also generically involves several other time scales, e.g., due to the early detachment from the shearing walls at large stresses, and that τ_f also depends on boundary conditions as well as on the preshear protocol or on external mechanical vibrations. For full details, the reader is referred to (Gibaud et al. 2010, 2016, 2020; Grenard et al. 2014; Perge et al. 2014; Helal et al. 2016).

Caseinate Gels as Model Materials for Irreversible Yielding

The counterpart of Fig. 5a–c for sodium caseinate gels is displayed in Fig. 5d–f. Here again, the strong time- and load-dependence of the yielding process is evident. In the creep experiments of Fig. 5d, the shear rate first decreases as a power law of time $\dot{\gamma} \sim t^{-\alpha}$, with $\alpha \simeq 0.85$. This initial regime is strongly reminiscent of the primary creep regime observed in hard solids (Miguel et al. 2002; Nechad et al. 2005; Rosti et al. 2010) and referred to as “Andrade creep” (da C Andrade 1910). Here, the value of α observed in sodium caseinate gel can be inferred from linear viscoelasticity (Leocmach et al. 2014), and quantitatively differs from the value 2/3 classically reported in hard solids, where such a primary creep response is interpreted in terms of collective plastic events (Miguel et al. 2008). Then $\dot{\gamma}$ reaches a minimum and finally diverges at the fluidization time τ_f . In the fatigue experiments shown in

Fig. 5e, the strain increases slowly before diverging upon yielding, which defines the fluidization time τ_f . The striking divergence of $\dot{\gamma}(t)$ and $\gamma_0(t)$ is the hallmark of irreversible rupture in the investigated sodium caseinate gels. Contrary to the case of reversible yielding where a saturation is observed, the velocity of the moving tool keeps increasing for all applied stresses until the rheometer reaches its speed limit. In the process, the gel structure is fully destroyed. Moreover, the gel does not recover once the load is released, which is why τ_f corresponds to the “fracture time” (van Vliet and Walstra 1995). As a consequence, one has to perform the various yielding tests on different samples, each being freshly prepared for a given set of parameters.

Furthermore, as displayed in Fig. 5f, the rupture time does not follow an exponential scaling but its dependence with stress is rather given by a power law, $\tau_f \sigma^{-\beta}$, with $\beta = 5.5$ under creep and $\beta = 4.2$ under fatigue. This power-law scaling was first reported for sodium caseinate gels by Leocmach et al. (2014) and is strikingly reminiscent of the Basquin law of fatigue (Basquin 1910) found for a variety of heterogeneous or cellular materials under cyclic deformation (Kohout 2000; Kun et al. 2008). This behavior can be recovered from a fiber bundle model where the system under stress is represented by a set of linear elastic fibers following simple failure rules (Jagla 2011). When the fiber bundle is subjected to an increasing external load, the fibers behave like linear elastic springs until they break for a given failure load. To recover the Basquin law, (Kun et al. 2008) modified the original fiber bundle model and considered a mean-field approach in which the network strands form a random network and fail either due to immediate breaking or to aging through damage accumulation. In this framework, β is directly related to the growth of local damage as a function of the local stress. High values of β mean that the material is prompt to accumulate damage. In soft gels, typical values of β range from 1 to 10, much larger than in hard solids such as metals ($\beta \simeq 0.1$) (Eshbach and Tapley 1990) and asphalt ($\beta \simeq 0.5$) (Kun et al. 2008). Here, the larger exponent found in creep tests than in fatigue experiments suggests that sodium caseinate gels accumulate damage

more “efficiently” under a constant stress than under an oscillatory stress. In any case, both the strain divergence during the approach of yielding and the Basquin power-law scaling for the rupture time are indicative of a brittle-like behavior of the strand network, which strongly differs from the delayed yielding observed in gels constituted of colloidal clusters. This difference is further explored through more local approaches in the next paragraph.

Characterizing Yielding Through Spatially-Resolved Dynamical Measurements

Measuring the functional form $\tau_f(\sigma)$ constitutes a big step forward when compared to the simple amplitude-sweep measurements or to the mere estimation of a yield stress or strain. In particular, the stress-dependence of the fluidization time allows one to classify the yielding behavior, to infer a rupture mechanism and to quantitatively test models, e.g., based on reversible bond-breaking or on damage accumulation. This approach remains however macroscopic and more local measurements are required to better pinpoint the rupture mechanism. Such measurements can be performed at different length scales: at the mesoscopic scale, typically 10–100 μm , in order to map the displacement field within the gel or at the microscopic scale, typically 0.1–10 μm , to directly retrieve the structure of the strands or clusters during fatigue or creep experiments.

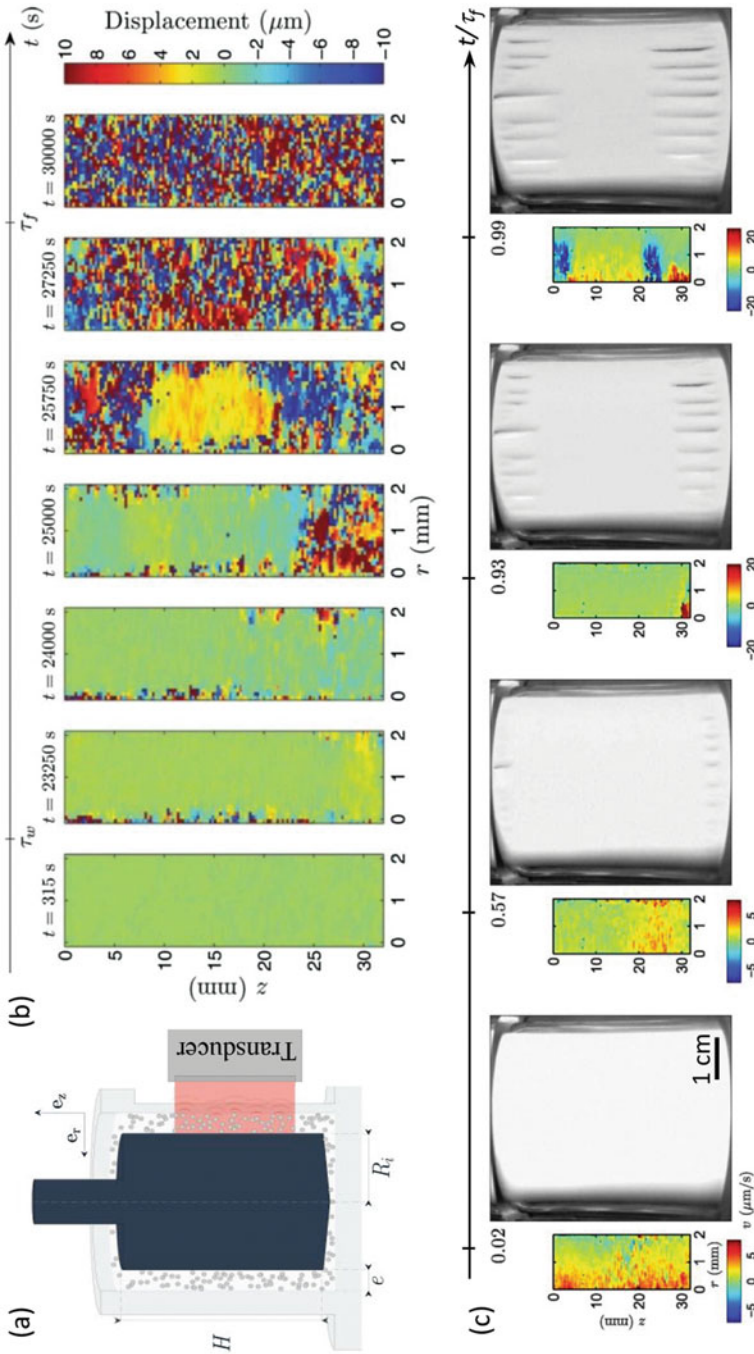
At the mesoscopic scale, displacement maps and velocity profiles can be obtained from scattering-based techniques (Adam et al. 1988; Kroon et al. 1996; Romer et al. 2000; Duri et al. 2005), magnetic resonance imaging (Assink and Kay 1991; Bonn et al. 2008), image correlation microscopy (Derks et al. 2004; Larsen and Furst 2008; Edera et al. 2017) or ultrasonic imaging (Manneville et al. 2004; Gallot et al. 2013; Saint-Michel et al. 2016).

When coupled to rheology, the latter high-frequency ultrasonic imaging technique, sketched in Fig. 6a, allows one to measure the displacement map within the gel with a spatial resolution of about 50 μm simultaneously to standard rheological observables. Compared to light-based techniques, ultrasound has the great advantage of

being able to probe optically opaque gels, in spite of lower spatial resolution. In the case of the carbon black and sodium caseinate gels investigated so far, which are transparent to ultrasound, this imaging technique necessitates to seed the gel with acoustic contrast agents, respectively hollow glass spheres of mean diameter 6 μm and polyamide spheres of mean diameter 30 μm .

Figure 6b shows displacement maps recorded during a fatigue experiment carried out on a carbon black gel. One can identify four successive regimes. (i) At short time scales, the gel displacement from one oscillation cycle to the other is zero, i.e., the gel behaves like an elastic solid. (ii) For $t = \tau_w$, the gel yields at the inner cylinder of the geometry (located at $r = 0$) inducing a plug-like flow of the bulk gel. (iii) The gel gets progressively fragmented into large solid domains (that show as uniform patches on the displacement map) evolving in a fluid background (that shows as apparently noisy regions where the displacements are very large and uncorrelated from one pixel to the other). (iv) Finally, at $t = \tau_f$, those large domains get fully eroded, and the whole gel is turned into a homogeneous fluid. As described in detail in (Perge et al. 2014; Gibaud et al. 2016), this last step corresponds to the final increase in the strain amplitude γ_0 reported in Fig. 5b.

Thus, despite a complex yielding process characterized by solid-liquid coexistence and heterogeneous flows, the carbon black gel ends up being homogeneously fluidized. The case of a sodium caseinate gel is strikingly different. Figure 6c shows pictures of the gel subjected to a creep experiment in a concentric-cylinder cell together with time-resolved velocity maps. Three regimes are observed under a constant stress. (i) During primary creep, the gel is linearly deformed and behaves like an elastic solid. (ii) At intermediate times, around the time at which $\dot{\gamma}(t)$ reaches a minimum value in Fig. 5d, regularly-spaced cracks start to nucleate from the top and bottom edges of the cell. (iii) Finally, cracks grow along the vorticity direction, i.e., perpendicular to the applied stress, and the gel eventually fails when fractures meet in the middle of the cell at τ_f , which translates into the divergence of the shear rate. The macroscopic fractures within the sodium



Nonlinear Mechanics of Colloidal Gels: Creep, Fatigue, and Shear-Induced Yielding. Fig. 6 Heterogeneous dynamics during yielding of carbon black and sodium caseinate gels. (a) Sketch of the rheology experiment coupled to high-frequency ultrasonic imaging. The rheology is carried out using a Taylor-Couette geometry, a concentric-cylinder geometry of height H and of gap e with an inner rotating cylinder of radius R_i . (b) Time-resolved displacement maps $\Delta(r,z,t)$ recorded in a carbon black gel at 6 wt % in light mineral oil between two cycles of oscillation during a fatigue experiment with $\sigma_0 = 11$ Pa and $f = 1$ Hz. (Adapted from Perge et al. (2014) with permission from the Society of Rheology.) The experiment is performed in the experimental setup sketched in (a) with $H = 50$ mm, $e = 2$ mm and $R_i = 48$ mm. r denotes the radial distance from the inner cylinder and z the position along the height of the cylinder.

τ_w indicates the time at which the gel detaches from the inner cylinder and τ_f indicates full bulk fluidization, which corresponds to the last inflection point of $\gamma_0(t)$ in Fig. 5b. (c) Typical fracture growth in a sodium caseinate gel at 4 wt % acidified with 1 wt % GDL and subjected to a constant shear stress $\sigma = 300$ Pa in the experimental setup sketched in (a) with $H = 60$ mm, $e = 2$ mm and $R_i = 23$ mm. The picture taken at $t/\tau_f = 0.57$ corresponds to the time at which the shear rate passes through a minimum. Velocity maps $v(r, z, t)$ recorded simultaneously to both the rheological data and to the images are shown next to the corresponding picture. (Adapted from Leocmach et al. (2014) with permission from the American Physical Society.) τ_f is the “fracture time” defined from rheology as the point where $\dot{\gamma}(t)$ diverges in Fig. 5d and which also corresponds to when fractures meet in the middle of the cell

caseinate gel network are invaded with water expelled from the gel matrix. Therefore, the yielding behavior of the present acid-induced protein gel can be described as a stress-induced macroscopic fracture of the gel network leading to an irreversible separation of the sample between a dilute protein suspension and broken pieces of the original gel.

To summarize, we have illustrated how reversible and irreversible yielding processes differ at both macroscopic and mesoscopic scales based on optical and ultrasound imaging. Note that the gel microstructure under stress can also be probed at scales below 10 μm by coupling the shearing device to scattering techniques such as small-angle neutron, x-ray or light scattering (Verduin et al. 1996; Pignon et al. 1997; Varadan and Solomon 2001; Mohraz and Solomon 2005; Vermant and Solomon 2005; Eberle and Porcar 2012; Kim et al. 2014; Hipp et al. 2019). When time-resolved measurements are available, such techniques provide valuable insight into the yielding dynamics in the reciprocal space, i.e., as a function of the scattering wave number. For instance, they allow one to identify the relevant length and time scales of plastic activity (Aime et al. 2018). However, they fail to provide a direct picture of the microscopic mechanisms underpinning the physics of shear-induced yielding in colloidal gels. As discussed below in section “Can We Get a Microscopic Picture of Yielding?,” fast confocal microscopy appears as an even more promising alternative to tackle such a challenge.

Fundamental Questions and Perspectives

In the previous sections, we have illustrated how one may investigate the yielding transition on two specific cases representative of two distinctive behaviors, namely reversible fluidization and irreversible fracture. Such a distinction opens a number of fundamental questions, e.g., on the predictability of yielding or on the microscopic rupture events pre-existing macroscopic failure. In the following section, we list such questions and draw a few perspectives for future work.

What Is the Physical Meaning of the Functional Form $\tau_f(\sigma)$?

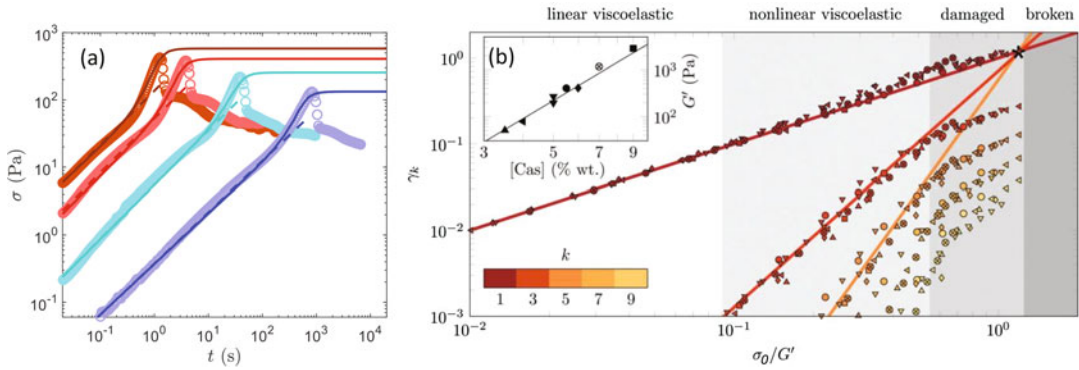
We have identified two types of functional forms for the empirical failure law $\tau_f(\sigma)$, namely an exponential in the case of carbon black gels, and a power law in the case of sodium caseinate gels. The reason for such a striking difference and the physical origins of these laws remain unclear and raise several outstanding questions.

First, does such a difference at the macroscale directly stem from the fact that bonds can spontaneously reform in carbon black gels, whereas they cannot in sodium caseinate gels, or does it originate only from stress-induced plastic events at the microscale? In that framework, one may ask whether precursors to failure are of different nature for these two functional forms, and thus if they could help anticipate the nature of the failure scenario thanks to a single creep or fatigue experiment. Second, one may be tempted to rationalize these two functional forms as two cases of a single master function $\tau_f(\sigma)$ that could involve a Weibull distribution for instance (van der Zwaag 1989). This raises the question of whether it is possible to go continuously from one type of functional form to the other within the same type of colloidal gel and how to devise such an experimental system.

How Does Strain-Induced Yielding Compare to Stress-Induced Yielding?

So far, we have focused on stress-induced yielding through both creep and fatigue experiments. Another way to induce yielding is by imposing a constant *shear rate*, $\dot{\gamma}$, in a shear start-up experiment as sketched in Fig. 4d. Such a flow test amounts to submitting the material to a shear strain $\gamma(t) = \dot{\gamma}t$ that increases linearly with time. As long as the deformation lies in the linear domain, imposing the strain is equivalent to imposing the stress. However, such an equivalence a priori breaks down when the material enters the nonlinear regime so that a natural question is how yielding under a given shear rate may be compared to that induced by stress and whether it is possible to relate the two.

Figure 7a shows the stress responses of a sodium caseinate gel during shear start-up experiments performed under various shear rates. The



Nonlinear Mechanics of Colloidal Gels: Creep, Fatigue, and Shear-Induced Yielding, Fig. 7 (a) **Strain-induced rupture.** Shear stress response σ vs. time t of a sodium caseinate gel at 4 wt % acidified with 1 wt % GDL and subjected to a constant shear rate $\dot{\gamma} = 10^{-3}, 0.02, 0.2$ and 0.6 s^{-1} (from right to left) applied at $t = 0$. The fracture time T_f corresponds to the locus of the stress maximum. Dashed lines correspond to linear viscoelastic response and solid lines show the K-BKZ prediction. (Adapted from (Keshavarz et al. 2017) with permission of the American Chemical Society.) (b) **Rupture prediction from Fourier transform rheology.** Amplitude of the Fourier modes γ_k of the strain response of sodium caseinate gels subjected to an oscillatory stress of amplitude σ_0 for various casein

concentrations. Colors code for $k = 1$ to 9. The stress amplitude is normalized by the elastic modulus G' of the gel measured in the linear viscoelastic regime. Solid lines show the best power-law fits of γ_k for $\sigma_0/G' < 0.5$. The build-up of Fourier modes within the nonlinear viscoelastic regime yields an empirical criterion for rupture as the intersection point of the power-law extrapolations into the damaged regime. Inset: elastic modulus G' as a function of the sodium caseinate weight concentration $[\text{Cas}]$. Symbols code for casein concentrations in the main graph. The solid line is $G' \sim [\text{Cas}]^4$. (Adapted from Saint-Michel et al. (2017) with permission from the Royal Society of Chemistry)

general shape of σ vs. t resembles that of σ_0 vs. γ_0 reported in Fig. 3b. In particular, it presents a marked stress increase characteristic of strain stiffening prior to the sudden drop that marks the sample macroscopic failure. As explained at length in (Keshavarz et al. 2017), such stress responses can be quantitatively modeled by a K-BKZ (Kaye–Bernstein–Kearsley–Zapas) constitutive formulation (Bird et al. 1987; Larson 1999) based on the linear viscoelastic spectrum and a “damping function” inferred empirically from step-strain experiments. The predictions of this K-BKZ approach are displayed as solid lines in Fig. 7a and closely match the experimental data up to the rupture point. Interestingly, one may relate the fracture time $T_f(\dot{\gamma})$, which is now a function of $\dot{\gamma}$ since measured under a constant shear, to the Basquin law $\tau_f(\sigma)$ obtained from creep tests thanks to the Bailey “durability” criterion first introduced for glasses and metals (Bailey 1939; Freed and Leonov 2002) and later applied to the rupture of polymeric liquids and elastomers (Eirich and Smith 1972; Malkin and Petrie 1997).

This criterion states that $\int_0^{T_f} dt / \tau_f[\sigma(t)] = 1$, where the creep rupture time τ_f is evaluated all along the loading process $\sigma(t)$. The Bailey criterion assumes that the failure of the material results from the accumulation of independent local failure events. Combining the K-BKZ approach with the Bailey criterion allows one to quantitatively predict the scaling of the yield stress and yield strain as a function of the applied shear rate $\dot{\gamma}$. This result nicely extends the range of application of Bailey’s criterion to soft viscoelastic gels, further reinforcing the emerging analogies between soft and hard materials (Schmoller and Bausch 2013).

Still, the above approach to reconcile stress-induced and strain-induced failure requires a careful modeling of the linear and nonlinear viscoelastic response. In the specific case of sodium caseinate gels, it is successful thanks to a robust, well-defined kernel for the K-BKZ equation. Besides, in these gels, the deformation remains homogeneous well into the nonlinear viscoelastic regime without significant structural damage. In practice, however, the gel may detach from the

wall and/or present heterogeneous deformation fields, as already shown above in Fig. 6b in the case of carbon black gels. Therefore, it is not clear whether a similar approach, possibly based on a different durability criterion, is achievable in the case of reversible, delayed yielding due to activated processes, or even in other colloidal gels showing irreversible, brittle-like rupture. Finally, the Bailey criterion necessitates previous knowledge of the full $\tau_f(\sigma)$ law and, as such, does not allow one to become genuinely predictive of rupture. This observation leads us to ask whether it is at all possible to predict yielding in colloidal gels based on the sole measurement of macroscopic rheological observables.

Can One Predict the Yielding Scenario from Macroscopic Observables?

Rupture prediction consists in using indicators of the material properties way before it fails to predict the time, strain, or stress at which the sample will fail. Establishing a yielding prediction from the sole rheological measurements appears as a major challenge for colloidal gels. Leocmach et al. (2014) have shown that the time $\tau_{\min}$ at which the shear rate reaches its minimum in the creep experiments of Fig. 5d is the same fraction of the rupture time τ_f whatever the applied stress, namely $\tau_{\min} \simeq 0.57\tau_f$. Such a proportionality is known as the Monkman-Grant relation (Monkman and Grant 1956; Voight 1989) and has been reported in a broad variety of solids (Sundararajan 1989; Nechad et al. 2005; Laurson et al. 2011). It allows for a rough estimate of the rupture time by recording $\dot{\gamma}(t)$ up to the point where it reaches a minimum. Still, sample to sample variations usually dominate, which limits the predictions of the failure time to within at least 10% (Koivisto et al. 2016). Moreover, as seen in Fig. 6c, at this point, macroscopic fractures have appeared, and the network structure is already deeply affected by stress.

For the same sodium caseinate gels, Fig. 7b shows that, based on Fourier transform rheology (Wilhelm et al. 2002), a prediction of rupture under an oscillatory stress can be empirically achieved before any significant damage occurs. There, we take advantage of the increasingly rich

harmonic content of the strain response to an oscillatory stress of increasing amplitude (Saint-Michel et al. 2017). The strain response is decomposed into a Fourier series, $\gamma(t) = \sum_k \gamma_k \cos(2\pi kft + \phi_k)$, where γ_k is the amplitude of the k th harmonics and ϕ_k its phase with respect to the sinusoidal stress input $\sigma(t) = \sigma_1 \cos(2\pi ft)$, which is applied for only 10 cycles of oscillations and for increasing amplitude σ_1 . Between two sets of oscillation cycles, the gel is left to recover for 10 min. The amplitudes of the harmonics $\gamma_k > 1$ follow power laws of the applied stress amplitude with exponents that increase with k and that are larger than 1 in the non-linear viscoelastic regime and eventually get close to 1 in the damaged regime. The extrapolations of the power laws from the non-linear viscoelastic regime all intersect at a single point. Interestingly, this single point matches remarkably well the experimental rupture point ($\sigma_c/G' = 1.06 \pm 0.25$, $\gamma_c = 1.32 \pm 0.20$). This empirical analysis seems to point out that rupture is encoded in the non-linear strain modes and that, for sodium caseinate gels, a simple extrapolation of Fourier modes allows one to *predict* the rupture point way before the gels actually fail. Such an idea echoes findings from Fourier transform rheology on other systems such as polymer melts (Hirschberg et al. 2017).

Here again, the fact that the deformation field remains homogeneous and that the gel sticks to the walls deep into the nonlinear regime might help to get a simple rupture prediction in the present protein gel. Furthermore, in the absence of any theoretical basis, such a prediction appears as an ad-hoc criterion, and more work is needed to understand its origin. Whether or not a similar predictive approach, either based on Fourier modes or on more advanced indicators from LAOS measurements (Ewoldt et al. 2008; Dimitriou et al. 2013), can be proposed for reversible yielding of colloidal gels stands out as an open question.

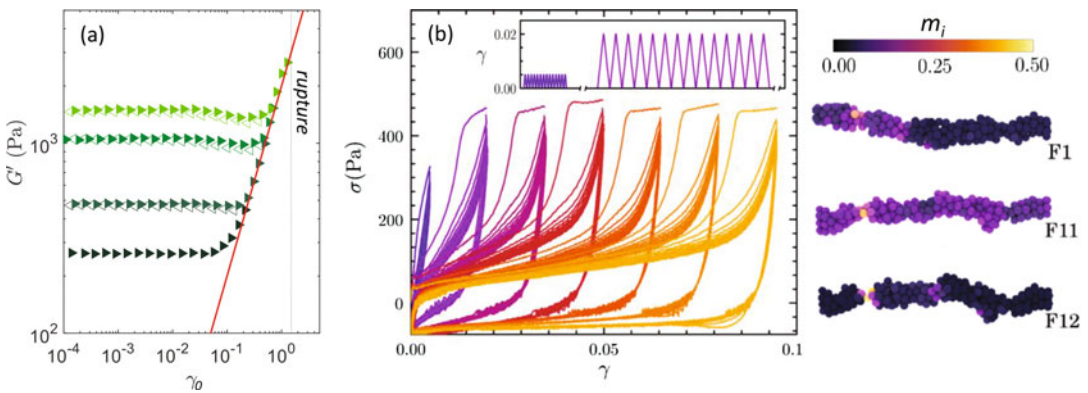
What Does Strain-Stiffening Tell Us About Yielding?

Related to the previous question of the yielding predictability is the observation that colloidal gels do not all become weaker before rupture.

Although strain softening corresponds to the most general case, as exemplified in Fig. 3a for carbon black gels, some gels show the reverse trend. Indeed, their elastic modulus G' increases as the strain or stress increases, i.e., these gels stiffen until abrupt rupture takes place. Such a strain-stiffening behavior has also been reported in a wide range of materials including rubbers, swollen polymer gels and semi-flexible biopolymer networks such as actin (Gardel et al. 2004; Schmoller et al. 2010), heat-set β -lactoglobulin (Pouzot et al. 2006), collagen (Arevalo et al. 2015), fibrin, and vimentin or neurofilaments (Storm et al. 2005). In colloidal gels, strain stiffening is rather rare and, when present, the amplitude of the phenomenon is usually small with G' increasing at most by a factor of 5. This is the case for polystyrene latex particles that gel under the addition of MgCl_2 (Gisler and Weitz 1999) or for the sodium caseinate gels that we have been discussing throughout in this article, as displayed in Fig. 3b. Recently, however, it was reported that natural rubber latex gels (de Oliveira Reis et al.

2015) and thermosensitive polystyrene colloidal gels (van Doorn et al. 2018) display a strain-stiffening behavior with an amplitude comparable to that of biopolymer gels for which G' may increase by a factor of 100. As shown in Fig. 8a and b, the elasticity of these gels adapts to the imposed stress or strain and grows up to rupture.

The interpretation of such an impressive strain stiffening and its relationship with subsequent yielding are not yet settled. Using numerical simulations, van Doorn et al. (2018) suggest that plasticity at the strand level is responsible for the strain-stiffening behavior. Mechanical loading leads to strand stretching, which displays a strong hysteresis: it builds slack into the network that softens the solid at small strains but causes strain stiffening at larger deformations. Bouzid and Del Gado (2017) have recently tackled this issue through computer simulations and found that strain stiffening could be understood in terms of backbone network topology: the stiffening is observed in stiffer gels where there is a lack of soft bending relaxation modes. Those gels exhibit



Nonlinear Mechanics of Colloidal Gels: Creep, Fatigue, and Shear-Induced Yielding, Fig. 8 Strain stiffening prior to rupture. (a) Response of a natural rubber latex colloidal gel at a volume fraction of 0.11 to successive amplitude sweeps under oscillatory shear. Each cycle consists of a continuous increase in strain amplitude γ_0 (full symbols) up to a predetermined maximum strain $\gamma_{\max}$, followed by a continuous decrease in strain amplitude (empty symbols). Each new cycle is performed on the same sample. The elastic modulus increases irreversibly until rupture at $\gamma_c \simeq 1.3$. The red line highlights the strain stiffening behavior the gel, $G' \sim \gamma_0^{1.0}$. (Adapted from de Oliveira Reis et al. (2019) with permission from the Royal

Society of Chemistry.) (b) Stress-strain curves $\sigma(t)$ vs. $\gamma(t)$ of an attractive polystyrene gel at a volume fraction of 0.18 for a triangular strain input with $\dot{\gamma} = 0.1 \text{ s}^{-1}$ and increasing values of the maximum strain $\gamma_{\max} = 0.005, 0.02, 0.035, 0.05, 0.065, 0.08, 0.095$ (from blue to yellow, see also inset). The right panel shows visual representations of the plastic deformation in a computer-simulated gel strand after the first cycle (F1), before fracture (F11), and after fracture (F12). Colors code for low (purple) to high (yellow) noncumulative plastic deformation m_i per particle. (Adapted from van Doorn et al. (2018) with permission from the American Physical Society)

purely stiffening behavior due to their still relatively sparse backbone connectivity that allows for stretching and orienting the gel branches along the direction of maximum elongation in shear.

Still, natural rubber latex gels must fall in another category as the strain-stiffening process is irreversible (de Oliveira Reis et al. 2019): once stiffened the material never regains its initial elasticity. Here, it can be hypothesized that the network is not just stretched and oriented but that it restructures, most probably through strand coalescence along the shear direction. Another interpretation could rely on the details and specificity of the particles themselves. In any case, it is clear that the strain-stiffening phenomenon that precedes rupture deserves renewed attention as it may help discriminate between various plastic responses or restructuring processes in some colloidal gels.

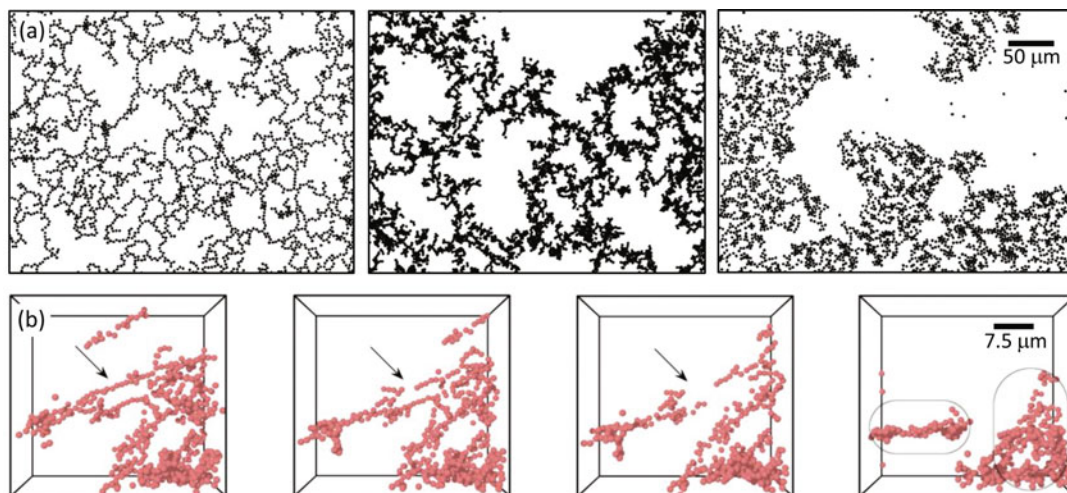
Can We Get a Microscopic Picture of Yielding?

As already pointed out above in section “[Characterizing Yielding Through Spatially-Resolved Dynamical Measurements](#),” macroscopic observables such as rheological data, although very informative, do not tell us anything about the microscopic events that govern yielding in colloidal gels. Therefore, additional experimental tools are needed to explore yielding at the cluster or strand scales. To be able to anticipate failure, one needs to identify *precursors* of yielding both for reversible and irreversible yielding. Such precursors are broadly defined by Cipelletti et al. (2020) as “any sharp variation of a parameter quantifying the system structure or dynamics on length scales of the order of, or slightly larger than, the relevant length scale of the sample structure, [and that] should be detectable well in advance of macroscopic failure.” A major step forward has been achieved recently by Aime et al. (2018) in the case of a gel of silica colloids that shows irreversible rupture. By coupling rheometry to small-angle light scattering, it was shown that the minimum in the shear rate corresponds to a sudden burst of plastic activity that is interpreted as the proliferation of irreversible rearrangements most probably consecutive to bond-breaking events.

This dynamic precursor irreversibly weakens the network until it fully breaks.

Although very promising, the previous dynamic light-scattering technique still fails to provide detailed, spatially-resolved information on the individual events that are responsible for plastic activity. To access such information, direct microscopic visualization must be performed. To date, only a handful of studies have addressed this question in colloidal gels. In particular, monolayers of attractive colloidal particles trapped at an liquid–gas interface or at a liquid–liquid interface have allowed one to image model two-dimensional gels with video microscopy under strain or stress and to study flow-induced anisotropy in the aggregated layer (Hoekstra et al. 2003; Vermant and Solomon 2005). It was shown by Masschaele et al. (2009, 2011) that yielding is preceded by a cascade of bond-breaking events, which number steadily increases up to a strain $\gamma \sim 1$. Dangling chains that are formed upon breaking may either fold back to the backbone or reconnect with other dangling ends. In the former case, the backbone densifies while connectivity is restored in the latter case. For $\gamma > 1$, global connectivity is lost, and one is left with a more heterogeneous structure than that of the gel at rest, with larger voids that coexist with more compact clusters as illustrated in Fig. 9a.

In three-dimensional gels, confocal laser scanning microscopy (CSLM) as emerged as a powerful tool to study colloidal gels under flow (Prasad et al. 2007). Pioneering experiments by Varadan and Solomon (2003) on thermoreversible gels of silica colloids showed that squeeze flow induces voids at moderate volume fraction ($\phi = 0.26$) and cracks at large volume fraction ($\phi = 0.40$). In both cases, the characteristic size, i.e., void diameter or crack width, measured after flow cessation corresponded to about 10 particle diameters. Subsequent studies by (Tolpekin et al. 2004; Conrad and Lewis 2008) used faster CSLM to investigate the dynamic balance between aggregation and breakup events in depletion-induced gels of silica colloids under shear. More recently, the microstructure of colloidal gels made of poly(methyl-methacrylate) (PMMA) particles was imaged after imposing high-rate step strains,



Nonlinear Mechanics of Colloidal Gels: Creep, Fatigue, and Shear-Induced Yielding, Fig. 9 Shear-rate-induced rupture at the microscopic level. (a) Microscopy images of a two-dimensional colloidal gel composed of 3.1 μm polystyrene particles adsorbed at an oil-water interface with a surface fraction of 0.3. From left to right: gel structure observed just after aggregation and during steady-state flows at $\dot{\gamma} = 0.015$ and 0.026 s^{-1} . Note that particles have been reduced by about 20% in size for better visualization. (Adapted from Masschaele et al. (2011) with permission from the Royal Society of Chemistry.) (b) Three-dimensional images reconstructed from a confocal

microscopy experiment of a gel composed of 1 μm sterically-stabilized PMMA colloids at a volume fraction of 0.035 in an index-matched solvent. Polymers were added to the dispersion to mediate an attraction between the colloids (depletion interactions) and form a gel. From left to right: time sequence of a local rupture event indicated by the arrow, which leads to the formation of two distinct clusters highlighted by circles. The imposed shear rate is $\dot{\gamma} = 0.07 \text{ s}^{-1}$. The total duration of the sequence is about 100 s. (Adapted from Rajaram and Mohraz (2010) with permission from the Royal Society of Chemistry)

showing that bond-breaking events result from the erosion of rigid clusters that persist far beyond yielding and provide some degree of elasticity to the ruptured gel (Hsiao et al. 2012).

In all these previous works, however, no time-resolved information on yielding could be extracted. To the best of our knowledge, the only time-resolved studies of yielding in colloidal gels under shear were performed by Rajaram and Mohraz (2010, 2011). There, fast CSLM allowed the authors to access the various stages of the shear-induced microstructure in depletion-induced gels of PMMA colloids. Although limited to a temporal resolution of a few seconds per confocal image, these experiments revealed that after a first regime where the structure turns from isotropic to oriented along the extensional component of the flow, yielding results from sporadic, local rupture events that sometimes lead to the formation of chain-like segments that eventually merge with the gel backbone as displayed in Fig. 9b. The

fully ruptured gel is constituted of dense, disconnected solid-like clusters that coexist with large voids, which is qualitatively consistent with the mesoscopic picture shown above in Fig. 6b for carbon black gels (Gibaud et al. 2010, 2016; Perge et al. 2014).

Finally, it appears that confocal microscopy has only been applied so far to colloidal gels that show reversible yielding. Exploring irreversible rupture in a time-resolved fashion at the particle or strand scale constitutes one of the major challenges for future research. Experimental setups designed to apply a given shear stress while imaging the structure, such as those developed by Chan and Mohraz (2013), Dutta et al. (2013), Aime et al. (2016), and Colombo et al. (2019), seem very promising to address this challenge, especially if coupled to a rheometer and if a spinning-disk confocal microscope is used in order to achieve even higher frame rates.

Summary and Conclusion

Long-term goals in the study of yielding in colloidal gels are multiple. One of them consists in classifying the rupture processes in relation with the properties of the gels. This “zoologist” approach is all the more complex that the features of colloidal gels depend on a myriad of parameters such as the interaction potential, the particle concentration, or the pathway taken to form the gel. Thus one issue is to determine the minimal level of description of the colloidal gels necessary to capture the yielding scenario. Here, we have described the current state of understanding of the nonlinear mechanical response of colloidal gels starting from experimental observations on two different systems that highlight the typical features of reversible fluidization and irreversible rupture. While carbon black gels display reversible fluidization preceded by strain softening and characterized by an exponential stress dependence of the yielding times, sodium caseinate gels show brittle rupture preceded by strain stiffening and failure times that depend on the load as power laws. Such a clear-cut distinction in the yielding behaviors prompts us to rationalize the nonlinear mechanics of colloidal gels based on their structure, in particular on their intermediate structures. Such an idea is supported by the fact that carbon black gels and sodium caseinate gels respectively display cluster- versus strand-based structures. This coarse-grained approach at the network level has the advantage to drastically diminish the number of parameters necessary to classify rupture, restricting it to cluster or strand properties, such as their size and their fractal dimension. In particular, it disregards the influence of parameters such as the colloid interactions, the colloid concentration and the gelation pathway. This could greatly simplify our understanding of rupture and set a simple basis for future theoretical and simulation work.

A more refined coarse-grained approach would consist in focusing on the particles. Such a “colloid physicist” approach has been followed in the early and current literature on colloid and protein dispersions and has allowed one to make fairly precise predictions about the phase behavior and

the static properties of such particles under well-defined solution compositions (Cardinaux et al. 2007; Gibaud and Schurtenberger 2009). Coarse-grained approaches at the particle level are, however, far from providing a complete description of the complexity of colloidal gels. Colloidal particles are indeed rarely perfect spheres; their interaction potentials are, in general, not isotropic and do not necessarily remain invariant as a function of pH, temperature, or concentration. For instance, carbon black particles are fractal aggregates that may penetrate one another at high concentrations. Sodium caseinate colloids have complex shape- and pH-dependent interactions that provide an original way to form gels starting from a fluid dispersion at equilibrium. Natural rubber latex gels, although very similar to standard latex particle gels, show unprecedented strain stiffening, which link with the reorganization of the microscopic network structure remains to be uncovered. Such spectacular properties, which make colloidal gels all the more versatile, are difficult to model and call for more refined approaches than simple coarse-graining, including complementary modeling based on polymer or macromolecular approaches. The limits of simple colloidal descriptions have been recently discussed in the case of globular proteins (Sarangapani et al. 2015; Stradner and Schurtenberger 2020). Similarly, disentangling the influence of colloid physics from the polymer or macromolecular aspects of the particle on the rupture properties of colloidal gels remains an open challenge and could be of great help to fine-tune the gel rupture behavior.

Therefore, beyond classifying yielding processes in colloidal gels, controlling and/or predicting their rupture appears as a major challenge for future work. There again, the adequate level of description is crucial. While mesoscopic measurements may help interpret macroscopic mechanical observations, direct visualization at the scale of individual strands or particles is essential to assess rupture precursors and localized events during yielding. We also emphasize that the discussions in this chapter may apply to a larger range of materials than just colloidal gels. Indeed, some features of shear-induced yielding reported here for colloidal gels

share a number of similarities with the rupture of polymer gels (Skrzeszewska et al. 2010; Tabuteau et al. 2009; Mora 2011; Erk et al. 2012; Thornell et al. 2014), elastomers (Ducrot et al. 2014), or hydrogels (Karobi et al. 2016; Bai et al. 2019), i.e., three-dimensional networks composed of macromolecules that are chemically or physically cross-linked. This suggests that either some specific details of the particle are irrelevant or that the ambivalent properties of the particles, half-way between colloids and polymer or macromolecules, are at the origin of this analogy. In any case, much work is still required before gel microstructures, nonlinear viscoelastic responses, and yielding scenarios are fully connected and explained. Such a research effort will help to design and optimize soft materials where yielding is fully part of the application, e.g., in food products or 3D printing, or where it should rather be avoided.

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Statistical Physics of the Yielding Transition

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Article Outline

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Glossary

Yielding transition Dense disordered materials undergo, just like crystalline materials, a yielding transition under large deformation protocols. After the first elastic response, these systems accumulate irreversible plastic deformation until they either fracture (hard glassy materials) or flow (yield stress fluids), depending on the material properties and preparation.

Local shear transformations Local structural changes that dissipate energy play a similar role for the deformation process in amorphous materials as defects in crystals. The globally accumulated plasticity can be divided in the occurrence of many such local shear transformations.

Elastic interactions The on average elastic surrounding medium reacts to local shear transformations with an elastic response to the locally deformed part. This elastic response is long range and can trigger other events to occur.

Mesoscopic scale for elastoplastic descriptions Beyond the microscopic scale corresponding to the scale of the constituents of the material (atoms, molecules, bubbles, and grains) and the macroscopic scale for which

continuum models can be developed, a mesoscopic scale can be defined as the scale corresponding to the typical inclusion size of the shear transformations. Beyond this scale, the elastic response of the surrounding material becomes scale free.

Avalanche dynamics In the slow driving limit, the local shear transformations organize into strongly correlated domains and the dynamics becomes strongly intermittent. Energy release and duration of these correlated events follow a power law behavior, similar to what is observed in earthquakes (Gutenberg Richter law). The scaling properties point toward the existence of out-of-equilibrium critical transitions in the framework of yielding.

Out-of-equilibrium phase transitions This is an analogue to the well-studied equilibrium phase transitions. One observes scale-free behavior for the relevant dynamically defined observables, and in analogy to equilibrium critical phenomena one can try to find generic behaviors close to criticality for classes of systems and scaling relations between the various exponents. However, one has to note that some analogies do not apply, because these systems are typically far from equilibrium and exhibit apart from the obvious fluxes of mass also fluxes in energy. In the case of deformed amorphous materials, energy is continuously injected in the system to perform the deformation protocol and the energy is dissipated on small scales. Even the limit of small deformation rates will still yield dynamics far from equilibrium, and novel out-of-equilibrium statistical theories and methods apply.

Transient dynamics In the early deformation stages, one can trace the stress response to an imposed deformation (stress-strain curve) or the deformation response in time to an imposed sudden step stress (creep curve).

Steady state dynamics In the long time limit, the probability distribution for the relevant observables, such as local mesoscopic stresses,

becomes stationary and the dynamics becomes time-translational invariant.

Flow curve For yield stress fluids, one can establish a flow curve given by the steady state average stress value for a given deformation rate, or the average deformation rate in the long time limit for a given imposed stress.

Shear localization When local shear transformations organize spatially into strongly deformed regions, this can be identified as shear localization. This can take the form of slip lines that can be characterized by dynamical heterogeneities and live on relatively short timescales. During the transient dynamics, shear localization can occur in form of transient shear bands. Shear localization can also be observed as a steady state feature for intrinsically unstable flows; this typically occurs when the local shear transformations lead to a local weakening of the material.

Introduction

Amorphous materials under deformation, such as hard glassy materials soft and granular matter like emulsions, foams, colloidal suspensions, or large-scale granular materials, exhibit a wide spectrum of nontrivial phenomena that not only elicit fundamental questions, but also bring about various practical challenges (Rodney et al. 2011; Bonn et al. 2017; Nicolas et al. 2018; Cipelletti et al. 2020). One of the major goals, in this context, is to develop a unique theoretical framework for transient phenomena like stress overshoots prior to yielding, e.g., in metallic glasses (Kawamura et al. 1999; Lu et al. 2003; Maaß et al. 2012) and soft materials (Amann et al. 2013; Divoux et al. 2011; Dzuy and Boger 1983; Rogers et al. 2010; Zausch et al. 2008; Sentjabrskaja et al. 2014; Koumakis et al. 2012a, b), delayed failure in creep experiments (Cipelletti et al. 2020; Chaudhuri and Horbach 2013; Sentjabrskaja et al. 2015), together with steady state properties for soft glassy materials, such as strongly nonlinear flow curves (Agoritsas and Martens 2017).

Some of these questions can be approached by traditional continuum-modeling techniques.

However, it is known that several yielding phenomena of amorphous materials are dominated by fluctuations, strongly correlated dynamics, disorder, and memory effects resulting from the microscopic reality. In these cases, bridging the dynamics on the microscopic scale with its counterpart, the complex macroscopic consequences, is a challenging task that requires the use of statistical physics-modeling approaches and tools.

In this context, there exist several interesting out-of-equilibrium transitions, which are accompanied by intermittent dynamics (Bonn et al. 2017; Nicolas et al. 2018). In the quasi-static yielding, relevant for hard amorphous materials, the systems undergo a transition upon increase of an externally applied deformation. They evolve from an elastic regime at small deformations, to a plastic flow-regime after reaching the so-called static yield stress (Varnik et al. 2004). The nature of this transition in the transient regime, potentially leading to strongly intermittent dynamics in form of avalanches (Combe and Roux 2000; Karmakar et al. 2010), has been investigated in the context of non-equilibrium phase transitions (Jaiswal et al. 2016; Leishangthem et al. 2017; Ozawa et al. 2018; Popović et al. 2018). A second well-studied transition in this context is the dynamic yielding transition, which is concerned with the steady flow regime at a vanishing but finite imposed shear rate. In this quasi-static driving regime, the materials exhibit a finite dynamic yield stress that can differ from the above defined static one (Varnik et al. 2004). The emerging critical dynamics in the steady flow of soft glassy materials in the vicinity of the dynamic yield transition has been extensively studied (Bailey et al. 2007; Talamali et al. 2011; Lin et al. 2014; Liu et al. 2016; Aguirre and Jagla 2018).

Soft disordered materials in form of yield stress fluids have in common that once deformed beyond their solid elastic regime they yield plastically toward a complex flow regime with a shear rate-dependent viscosity (Bonn et al. 2017; Nicolas et al. 2018). The steady state flow behavior of these yield stress fluids can be described at the continuum level using empirical laws like the Herschel-Bulkley relationship (Herschel and Bulkley 1926), or continuum descriptions, such as

viscoelastoplastic (Marmottant and Graner 2007; Saramito 2007) and fluidity models (Bocquet et al. 2009; Fielding 2014). While these types of descriptions account well for the average flow behavior at a coarse-grained scale, it has appeared that some flow features of yield stress materials are dominated by giant fluctuations of the macroscopic stress or shear rate (Coussot et al. 2002; Lootens et al. 2003; Cantat and Pitois 2006; Barés et al. 2017; Pastore et al. 2011; Srivastava et al. 2019). This can, for example, lead to nonlocal, strongly system-size-dependent, transport coefficients for the material dynamics (Lemaître and Caroli 2009; Martens et al. 2011; Tyukodi et al. 2018). Accordingly, understanding the role of mechanical noise and its spatiotemporal features has not only attracted a strong fundamental interest (Nicolas et al. 2018) but is also of direct importance in rheological applications (Bonn et al. 2017).

Part of the mechanical fluctuations in driven disordered materials are usually generated by the flow itself, for example, resulting from the elastic response of the material to localized plastic events (Argon and Kuo 1979; Schall et al. 2007). They are therefore very different in nature from thermally generated fluctuations (Nicolas et al. 2014) and must be incorporated into modeling approaches in a self-consistent manner (Hébraud and Lequeux 1998).

In some cases, flow-induced fluctuations can be associated with a self-fluidization of the material, i.e., a decrease in shear stress with increasing shear rate. This leads to nonmonotonic rheological constitutive curves (Fielding 2014; Schall and van Hecke 2010; Mansard et al. 2011) that can be associated with flow instabilities, potentially leading to shear localization, metastability, and hysteresis (Wortel et al. 2014). In the case of granular materials, this self-fluidization process finds its origin in sliding frictional contacts (Wortel et al. 2014, 2016; DeGiuli and Wyart 2017). In non-frictional yield stress materials, nonmonotonic flow curves can be explained by mechanisms such as inertia (Nicolas et al. 2016) or local softening following structural rearrangements (Coussot and Ovarlez 2010; Martens et al. 2012).

Besides this self-generated mechanical noise, there can be additional external sources of noise,

which can be regarded in a first-order approximation independent of the shear-induced one. This is, for example, the case of irreversible deformations induced by thermal activation (Chattoraj et al. 2010; Ikeda et al. 2012) or mechanical vibrations (D'anna et al. 2003; Caballero-Robledo and Clément 2009; Jia et al. 2011; Hanotin et al. 2012; Gnoli et al. 2016). Other mostly rate-independent fluctuations can also result from local processes such as coarsening in foams (Cohen-Addad et al. 2004), or internal activity (Mandal et al. 2016; Tjhung and Berthier 2017; Matoz-Fernandez et al. 2017). One important aspect of such external noise sources is that they can induce a fluidization of the system at small imposed external stresses. Interestingly, in the case of materials with a nonmonotonic constitutive curve, this additional fluidization can give rise to a critical point at finite deformation rates, which leads in the case of an imposed shear stress to giant fluctuations in the shear rate statistics (Wortel et al. 2016; Le Goff et al. 2019, 2020).

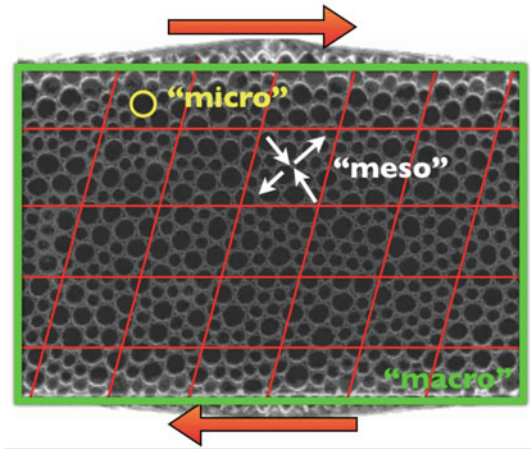
Elastoplastic Models

It is well established that deformation of disordered materials is realized through successive dissipative events in the form of localized shear transformations (Argon and Kuo 1979). These result in long-range elastic stress variations in the surroundings (Eshelby 1957a), potentially leading to cascading plastic events correlated on time and length scales far beyond the scale of the initial local rearrangement (Martens et al. 2011; Baret et al. 2002). Following this very generic picture, it has been proposed that brittle amorphous materials, such as metallic glasses, and dense soft particle flow, such as emulsions or colloidal suspensions, can be described by similar mesoscopic modeling approaches (Nicolas et al. 2018). To reveal the underlying physics and unify the understanding of the various phenomena in yielding and flow of amorphous systems, it is thus tempting to derive models on the mesoscopic scale, using coarse-grained quantities like a local tensorial stress, strain, and corresponding elastic moduli (Tsamados et al. 2009). A large number of elastoplastic descriptions are based on this understanding (Rodney et al. 2011; Nicolas et al. 2018;

Hébraud and Lequeux 1998; Baret et al. 2002; Merabia and Detcherry 2016).

To overcome fundamental difficulties related to the complexity of the dynamics on the microscopic scale, the elastoplastic modeling approach has been proposed to bridge the gap between the different scales (for an extensive review, see Nicolas et al. 2017). Built upon ideas developed by Argon and Kuo (1979), who pioneered the understanding that macroscopic plastic deformation in dense disordered materials is induced by localized plastic events of a size of few particle diameters, models were proposed starting from the scale of the typical plastic inclusion size (Baret et al. 2002; Bulatov and Argon 1994a, b), which implies an important coarse graining in space and in time. The dense particle system is divided into blocks of a size that is relevant to define a meaningful coarse-grained elastic modulus (Tsamados et al. 2009) together with fields of stress, elastic, and plastic deformation. The elastoplastic modeling approach depends crucially on the existence of these localized plastic events, and the approach can thus only be valid in deeply jammed systems since close to unjamming dissipation mechanisms are known to become strongly nonlocal (Lerner et al. 2012) (Fig. 1).

An elastically deforming region in the material acquires a new reference configuration not only as a response to the external deformation, but also responding to the surrounding plastically deforming regions. This new configuration will differ from the original reference state by some *eigenstrain*. To simplify the problem further, we consider that the plastically deforming zones can be considered point-like at this coarse-grained scale. In this limit, only the far field response of the surrounding material to the locally deformed plastic inclusions can be considered. In the simplest formulation, this response can be derived for linear isotropic elastic medium, which is a good first-order approximation of the complex problem. The mesoscopic model then involves the calculation of the elastic response of the surrounding medium to the forces that are exerted by the zones that have undergone a yield event. This calculation goes along the lines of a standard linear elasticity calculation, but we omit the details of this technical point and we give directly the final result that describes the response of the



Statistical Physics of the Yielding Transition, Fig. 1 Scheme of different scales: the microscopic scale (in yellow) on the scale of the constituents, here illustrated by the bubbles of a sheared polydisperse 2d bubble raft; the mesoscopic scale (in red) on the scale of the shear transformation inclusions; and the macroscopic scale (in green) is the scale of the average flow properties

medium at point $\vec{r}$ to a yield event taking place at the origin using the propagator $\mathcal{G}$ given in Eq. 1.

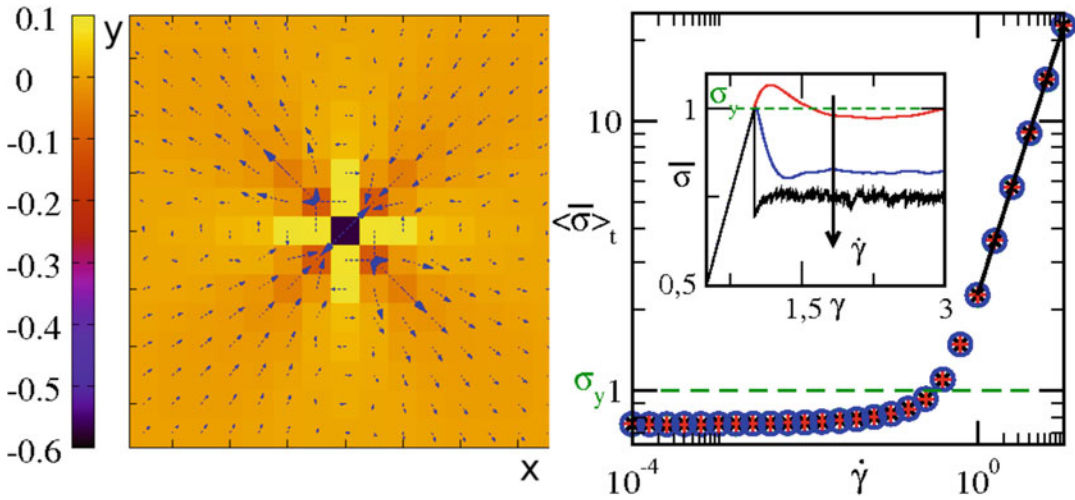
Approximating the rearrangements corresponding to the local plastic events by a force quadrupole (Eshelby problem), one expects a fourfold quadrupolar symmetry for the inhomogeneous part of the stress propagator (Eshelby 1957b). The form of this propagator for an infinite two-dimensional medium reads in nondimensional form

$$\mathcal{G}^{(\infty)}(r, \theta) = \frac{1}{\pi r^2} \cos(4\theta). \quad (1)$$

The medium is described by a set of elastoplastic elements that occupy the nodes of a regular square lattice. To model a yield stress material under steady shear with a fixed strain rate $\dot{\gamma}$, we start from a simple Maxwell-like description of the stress dynamics associated with a given element (Fig. 2):

$$\partial_t \sigma(t) = \mu \dot{\gamma} - 2\mu \dot{\epsilon}^{\text{pl}}(t) \quad (2)$$

where ∂_t denotes the partial time derivative, $\sigma(t)$ is the shear component of the stress tensor, μ is the shear modulus, and $\dot{\epsilon}^{\text{pl}}(t)$ accounts for the change in the strain due to local yielding. To take into



Statistical Physics of the Yielding Transition, Fig. 2 From microscopic events to macroscopic flow. *Left:* change in the stress field due to a single plastic event (color code) and the corresponding displacement field (blue vectors). *Right:* average local stress in the steady

state as a function of strain rate for different system sizes. Inset: evolution of the spatially averaged stress as a function of strain, the arrow indicates a decrease of the strain rate

account the long range effects of the plastic events, first predicted by Argon (Argon and Kuo 1979) and later evidenced in molecular dynamics simulations (Tanguy et al. 2006) and experiments on colloids (Schall et al. 2007), we change the above homogeneous equation to a field description with a stress propagator $G(\vec{r} - \vec{r}')$ accounting for the stress redistribution due to a plastic event,

$$\begin{aligned} \partial_t \sigma(\vec{r}, t) = & \mu \dot{\gamma} \\ & + 2\mu \int d\vec{r}' G(\vec{r} - \vec{r}') \dot{e}^{\text{pl}}(\vec{r}', t) \end{aligned} \quad (3)$$

To describe the deformation due to the plastic events, we model a Maxwellian viscoelastic-like relaxation of the material in the plastic state, i.e.,

$$\dot{e}^{\text{pl}}(\vec{r}, t) = \frac{1}{2\mu\tau} n(\vec{r}, t) \sigma(\vec{r}, t), \quad (4)$$

where τ is the typical time for the stress release in the plastic phase and $n(\vec{r}, t)$ a local state variable. In the following, we refer to $n(\vec{r}, t)$ as local activity. We define $n(\vec{r}, t) = 0$ indicating the absence of a plastic event and $n(\vec{r}, t) = 1$ if the local region is in the plastic phase.

To incorporate the idea of a yield stress, we define the following stochastic dynamics for the state variable $n(\vec{r}, t)$. If the local stress exceeds a threshold value $\sigma(\vec{r}, t) > \sigma_y$, there is a finite probability to yield locally. The yielding rate is given by $1/\tau_{\text{pl}}$. Once yielded, $(n(\vec{r}, t) = 1)$ stress is redistributed using an appropriate stress propagator, and locally the stress is relaxing during a typical restructuring time τ_{el} . The rate to reestablish the elastic state ($n(\vec{r}, t) = 0$) is given by $1/\tau_{\text{el}}$.

It has been shown that this very simplified cellular automata model, for the mesoscopic elastoplastic dynamics, results in many qualitative and semiquantitative results, fitting the fluctuations and rheological measurements from experiments and microscopic simulations. They have been intensively studied in the framework of dynamical heterogeneities (Martens et al. 2011), avalanche dynamics (Talamali et al. 2011), shear-banding (Martens et al. 2012), critical phenomena (Lin et al. 2014), and transient creep dynamics (Merabia and Detcherry 2016), to name only few fields where these types of models have been successfully used to understand the link between microscopic plasticity and the macroscopic mechanical response.

Mean-Field Descriptions

Several mean-field descriptions that neglect the details of the spatial dynamics have been developed. Examples are the soft glassy rheology model (Sollich et al. 1997; Moorcroft et al. 2011), fluidity models (Bocquet et al. 2009; Picard et al. 2002), the shear transformation zone theory (Falk and Langer 1998), and the mode-coupling theory (Fuchs and Cates 2002). Although some of these models could be successfully fitted to simulations and experiments (Zausch et al. 2008; Manning et al. 2007; Goyon et al. 2008; Mansard et al. 2013), the ingredients of these mesoscopic models remain in most cases phenomenological and the direct link to underlying microscopic dynamics remains unresolved. Due to the challenging character of the problem of deformation of disordered systems, no consensus has been established even on the basic ingredients that should underlie coarse-grained descriptions of the nonlinear rheological response of yield stress materials (Hébraud and Lequeux 1998; Sollich et al. 1997; Falk and Langer 1998; Agoritsas et al. 2015; Lin and Wyart 2016; Richard et al. 2020).

Here, we present in detail one of the ways to derive a phenomenological mean-field description that is based on the above lattice model. The idea is to introduce the probability density $\mathcal{P}$ of local shear stresses $\sigma = \sigma_{xy}$ in regions of mesoscopic size W while the material is sheared at rate $\dot{\gamma}$. The time evolution of $\mathcal{P}$ is given by

$$\partial_t \mathcal{P}(\sigma, t) = -G_0 \dot{\gamma}(t) \partial_\sigma \mathcal{P} - \frac{1}{\tau} \theta(|\sigma| - \sigma_c) \mathcal{P} + \Gamma(t) \delta(\sigma) + D(t) \partial_\sigma^2 \mathcal{P} \quad (5)$$

where $\theta(x)$ and $\delta(x)$ denote, respectively, the usual Heaviside and delta-distributions. The first term on the right-hand side proportional to the stress gradient of the probability density $\partial_\sigma \mathcal{P}$ accounts for the linear elastic response. The following term describes the loss in the probability density due to local yielding of overstressed regions above a critical stress σ_c at a rate given by $1/\tau$. It has been argued that the phenomenological parameter τ can be interpreted as the duration of a plastic event in the low shear rate limit (Agoritsas et al. 2015). The corresponding gain term is given in the

third expression on the right-hand side, where the stress is set to zero after a yielding event with a rate given by the plastic activity rate

$$\Gamma(t) = \frac{1}{\tau} \int_{|\sigma| > \sigma_c} \mathcal{P}(\sigma, t) d\sigma. \quad (6)$$

The last term encompasses the stress changes created through other yielding events in a mean-field manner, assuming that this mechanical noise can be approximated through a normal diffusion of the mesoscopic stresses. To describe this noise in a self-consistent manner, the HL approach proposes that its amplitude should be related to the rate of plastic activity through a dimensionless coupling constant $\tilde{\alpha}$

$$D(t) = \tilde{\alpha} \sigma_c^2 \Gamma(t). \quad (7)$$

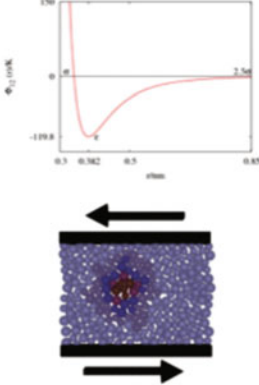
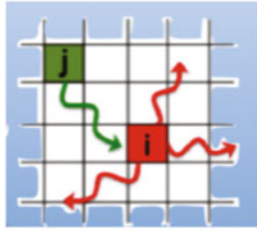
This last relation introduces a nonlinearity into Eq. (5), since the rate of plastic activity itself depends on the density probability of the mesoscopic stresses. It is this coupling that renders the problem nontrivial and yields interesting results regarding the behavior of macroscopic quantities.

This model is known to exhibit a unique stationary state for a finite shear rate in the large time limit, where the probability density for the mesoscopic stresses becomes time independent. To determine the time-averaged macroscopic stress in the steady state, one averages over the mesoscopic stresses weighted by the corresponding steady state probability density

$$\langle \sigma \rangle = \int \sigma \mathcal{P}(\sigma) d\sigma. \quad (8)$$

Using appropriate units, we can write the equations in dimensionless quantities, expressing stress-related values in units of the local yield stress σ_c , time quantities in units of τ , the shear rate in units of $\sigma_c/(G_0\tau)$, and the stress diffusion coefficient in units of σ_c^2/τ , leaving only two independent dimensionless model parameters that determine the flow behavior, namely the dimensionless shear rate and coupling constant $\tilde{\alpha}$.

The rheological results in the small shear rate limit for this model are well studied (Agoritsas

Micro	Meso	Macro
Particle simulations: <u>Bidisperse Lennard-Jones</u> <u>(Kob-Andersen model)</u> 	Lattice models: Simplistic model, e.g. for the study of critical dynamics 	Continuum or mean-field descriptions Neglect fluctuations and write continuum equations for the rheological relevant fields $\rho \frac{\partial v_x}{\partial t} = \frac{\partial \sigma}{\partial y} = \dots$

Statistical Physics of the Yielding Transition, Fig. 3 The different approaches for the different scales are illustrated in the above table

and Martens 2017; Hébraud and Lequeux 1998; Olivier and Renardy 2011). For small enough coupling strength $\tilde{\alpha} < 1/2$, the HL model predicts a Herschel-Bulkley flow behavior of exponent 1/2

$$\langle \sigma \rangle \approx \sigma_Y + A \dot{\gamma}^{1/2}$$

for the time-averaged macroscopic stress in the steady state $\langle \sigma \rangle = \int \sigma \mathcal{P}(\sigma) d\sigma$, with the two constants σ_Y (the dynamical yield stress) and A (the prefactor). Thus, this very simplified model can already capture well the nonlinear behavior of the flow of yield stress materials. Moreover, it has also been shown that the typical transient dynamics during creep experiments can be qualitatively well reproduced using these modeling techniques (Liu et al. 2018) (Fig. 3).

Conclusion and Outlook

Although much progress has been made in the statistical modeling of yield stress materials and their yielding phenomena, there remain still a lot of challenging questions. One important route is

to connect better the different scales by understanding how the mesoscopic parameters for the local yielding and initial conditions emerge from the microscopic interactions and preparation protocols (Liu et al. 2021).

In the recent past, there have been first steps toward a better understanding of the details in the elastic response to local shear transformations, the evolution of local yield thresholds (Puosi et al. 2015; Patinet et al. 2016), and the detection of precursors to local yielding events (Richard et al. 2020). This field became very active and is expected to develop rapidly in the future.

In a broader context, it will be important to understand the different links between the theory developed for the deformation of glasses with various interconnected fields. In the framework of aging and glassy dynamics, it will be important to connect the understanding of the deformation of glasses with the different theories about treating the dynamics close to the glass transition. For athermal systems, it will be important to connect the different insights with the knowledge in the field of jamming phenomena.

And last but not least, the yielding transition can serve as a model of an out-of-equilibrium system that remains close to applications. As such, it shows a variety of interesting out-of-equilibrium features, including critical dynamics, that can be studied within the general framework of out-of-equilibrium statistical physics.

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Granular Flows

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Article Outline

Glossary

Definition of the Subject

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Bibliography

Glossary

Granular matter a system comprised of a large number of grains, or particles, of macroscopic size. Examples include powders, sand, seeds, and the surface of Mars.

Granular fluid an activated (driven) state of granular matter such that the grains move (flow) and collide frequently.

Statistical mechanics a field of physics that addresses systems with many degrees of freedom based on the fundamental microscopic laws to describe derived macroscopic properties.

Macrostate a statistical description of a system with many degrees of freedom in terms of limited information about that system.

Hydrodynamic fields the local densities of mass, energy, and momentum defined at each point in the system of interest.

Normal state a macrostate whose time evolution is described entirely through that of the average hydrodynamic fields.

Balance equations exact equations for the time derivatives of the hydrodynamic fields in terms of associated fluxes and sources.

Constitutive equations expressions for the fluxes and sources of the balance equations as functionals of the hydrodynamic fields.

Hydrodynamics a macroscopic description of the system in terms of a closed, deterministic set of equations for the average hydrodynamic fields, resulting from the exact balance equations with approximate constitutive equations.

Navier–Stokes hydrodynamics local, first order in time, partial differential equations for states with small spatial gradients in the hydrodynamic fields (constitutive equations calculated to first order in the spatial gradients).

Definition of the Subject

The terminology granular matter refers to systems with a large number of hard objects (grains) of mesoscopic size ranging from millimeters to meters. Geological examples include desert sand and the rocks of a landslide. But the scope of such systems is much broader, including powders and snow, edible products such as seeds and salt, medical products like pills, and extraterrestrial systems such as the surface regolith of Mars and the rings of Saturn. The importance of a fundamental understanding for granular matter properties can hardly be overestimated. Practical issues of current concern range from disaster mitigation of avalanches and explosions of grain silos to immense economic consequences within the pharmaceutical industry. In addition, they are of academic and conceptual importance as well as examples of systems far from equilibrium.

Under many conditions of interest, granular matter flows like a normal fluid (Kadanoff 1999). In the latter case such flows are accurately described by the equations of hydrodynamics. Attention is focused here on the possibility for a corresponding hydrodynamic description of granular flows. The tools of nonequilibrium statistical

mechanics (McLennan 1989), developed over the past 50 years for fluids composed of atoms and molecules (Hansen and McDonald 1986; Resibois and De Leener 1977), are applied here to a system of grains for a fundamental approach to both qualitative questions and practical quantitative predictions. Applications of basic atomic physics principles to granular fluids have accelerated during the past decade, starting with an emphasis on molecular dynamics (MD) simulations (Goldhirsch et al. 1993) and kinetic theory (Brilliantov and Pöschel 2004; Dufty 2001), and more recently with the theoretical methods of the type described here (Brey et al. 1997; Van Noije and Ernst 2001; Dufty 2000; Dufty et al. 2002, 2006, 2007).

Introduction

To start with the familiar, consider a jar of vitamin pills, mustard seeds, or peanuts. Remove the lid and pour them into a bowl, observing that the “flow”, or their collective motion, has some similarity to that of a normal fluid such as water. The collective motion in both cases is the consequence of collisions among their constituents, grains or atoms, and their large number. It is tempting to make the correspondence of grains to atoms in considering the similarities of flows in these two types of fluids. The objective here is to explore in formal detail the extent to which that correspondence is conceptually and quantitatively justified. An important prerequisite is the integrity of the grains during their motion. Each grain is comprised of a large number of atoms or molecules. Integrity refers to their retention of mass and shape following interactions with other grains or with their environment. As such, the grains behave as “particles” whose detailed internal structure is not essential to their description, which is captured instead by a few parameters describing their shape, mass, and collisional properties with other grains. However, an important consequence of this underlying molecular structure is a redistribution of translational kinetic energy of the grains and internal energy of the constituent molecules. At the mesoscopic level

this appears as an energy loss on collisions between pairs of grains. This is a central feature of granular fluids differentiating them from atomic fluids: the inelasticity of granular pair collisions.

Granular matter occurs in two classes of states, compact and activated (see for example articles 2002). In the first case, the grains form a static packed configuration within the container due to the effects of gravity on their relatively large mass and their inelastic collisions. Any initial motion is quickly dissipated and their kinetic energy becomes negligible relative to the gravitational potential energy. Important questions arise about the possible and probable packing configurations that determine the stresses within the system and the distribution of forces on the container. For example, chains of particles in contact can occur as arches to support matter above them while reducing their force on the matter below. There is an intense interest in the study of such states, generically referred to as contact mechanics.

Activated states refer to continuously driven systems, or gravity free conditions. For example, a container of grains in a compact configuration can be shaken to impose kinetic energy and motion among the grains. Similarly, unrestrained systems in a gravitational field will flow towards lower potential energy (e.g., hopper flow or flow down an incline). Initial activation in space laboratory experiments provides another example (self-sustained fluidization). For the flows considered here as candidates for a hydrodynamic description continual collisions are essential. This means that within each small cell, still containing many particles, the particles are moving randomly relative to the collective motion of that cell. Thus, ballistic motion or beams with all particles moving independently in the same direction are excluded.

Both compact and activated grains may occur immersed in a continuum such as water or air that may have a strong or weak effect on their collective properties. For compact systems water may provide a lubrication effect that affects the dominant class of configurations. For activated systems it can provide an additional dissipative drag between collisions among the grains. When the

medium plays an important role the systems is said to be wet. In the opposite limit it is said to be dry. Finally, it is possible for compact and activated components of a system to coexist as heterogeneous states. Here, only the simplest case of dry systems in fully activated flows are considered. These are referred to in the following as granular fluids.

Advances in the study of granular fluids have arisen from many communities, including chemical engineering, materials sciences, and physics. The additional academic and conceptual importance of granular matter as practical systems for exploring the relevance of many-body fluid methods is primarily for the physics community. Granular matter, viewed as a system of particles with inelastic interactions, provides new opportunities to test the qualitative and quantitative limits of many-body methods developed over the past century for atomic and molecular systems. This is the field of non-equilibrium statistical mechanics (McLennan 1989; Hansen and McDonald 1986; Resibois and De Leener 1977). Granular matter provides a new testing ground for a reconsideration of the most fundamental concepts and tools (Kadanoff 1999), with the potential for enhanced understanding of their place in atomic and molecular systems as well.

Statistical mechanics addresses the difficult many-body problem of extracting macroscopic properties of experimental interest from the very large number of constituent particles. The results express these properties in terms of the fundamental “microscopic” features of these particles, such as mass, shape, degree of inelasticity, and collisional properties. In this way the properties of the vitamin pills, mustard seeds, and peanuts are distinguished at a fundamental level. Also, conceptual issues such as the limitations of a macroscopic description are exposed through the insistence on their logical evolution from the fundamental microdynamics. In the next section, the granular fluid is described as a system of particles interacting via pairwise additive, nonconservative forces. The microscopic dynamics of these particles leads to balance equations for the mass density, energy density, and momentum density. Their averages define the “hydrodynamic fields” which

are candidates for a macroscopic, continuum mechanics description. These exact equations are described in section “[Macroscopic Balance Equations](#)” and the need for “constitutive equations” to provide a closure is described. The origin of constitutive equations, and consequently the origin of hydrodynamics, is associated with the concept of “normal states” (Dufty and Brey 2005a) in section “[Normal States and Hydrodynamics](#)”. The normal state for the case of small spatial deviations from homogeneity is constructed formally in section “[Navier–Stokes Approximation](#)”, resulting in the constitutive equations for Navier–Stokes hydrodynamics (Here the Navier–Stokes [n.d.](#)). This derivation also provides insight into the context in which such a description should hold, and differences from the corresponding results for a normal fluid are noted. Empirical evidence (Huan et al. 2004; Bizon et al. 1999), simulations (Brey et al. 1999, 2002, 2005), and corresponding results from kinetic theory (Brey et al. 1998; Dufty 2005; Dufty and Brey 2002, 2005b) support the applicability of this hydrodynamic description under appropriate conditions. Finally, the results are summarized in section “[Future Directions](#)” and some comments on the outlook for future developments are offered.

The presentation here is focused on recent work of the author and his collaborators for application of statistical mechanics to explore hydrodynamics for a granular gas. Consequently, the references quoted are heavily weighted toward those developmental studies. Apologies are offered for the exclusion of the vast and important complementary literature on simulations, kinetic theory, and experiments also bearing on this topic. Many of these can be found in the list of Books and Reviews given here.

Granular Fluid and Its Statistical Mechanics

Nonequilibrium Statistical Mechanics

Consider a system of $N \gg 1$ identical grains (hereafter referred to as particles) in a volume V , whose initial positions $\{\mathbf{q}_i\}$ and velocities $\{\mathbf{v}_i\}$, $1 \leq i \leq N$, are specified. The positions and

velocities define a point in a $6N$ dimensional space denoted by $\Gamma \equiv \{\mathbf{q}_i, \mathbf{v}_i\}$, defining the microstate of the system. A macrostate is defined by a probability density $\rho(\Gamma)$ in this space, representing statistical rather than precise knowledge of the system. The field of statistical mechanics addresses properties of macrostates, based on the recognition that for very large N the details of microstates are neither experimentally accessible nor practically calculable. Properties of interest are represented by functions $A(\Gamma)$, and their values for a macrostate $\rho(\Gamma)$ are determined from the expectations

$$\langle A; \rho \rangle \equiv \int d\Gamma \rho(\Gamma) A(\Gamma). \quad (1)$$

In this section, a brief overview of the essential ingredients of nonequilibrium statistical mechanics is given, broadened from its usual form (McLennan 1989) to include granular matter.

The dynamics of macrostates is determined from the underlying dynamics of the microstates. The initial point Γ changes in time since the particles have velocities and move to new positions. They move in straight lines until one or more come within the force field of other particles, at which point their velocities change as well as their positions. The forces are taken to be pairwise additive, such that the total force on particle i is $\mathbf{F}_i = \sum_j \mathbf{F}_{ij}$, where $\mathbf{F}_{ij}$ is the force on particle i due to particle j . This does not mean that the interactions are pairwise sequential; three or more particles can interact simultaneously. The pair forces are restricted by Newton's third law, $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$, with conservation of momentum. Otherwise quite general forces can be considered to represent the shape of the particles and their degree of inelasticity. It is assumed here that the force range vanishes outside a distance $\sigma/2$ from the center of each particle so that σ characterizes the size of the particles. Furthermore, the particles are taken to be strongly repulsive so that their mean maximum overlap D on collision is small compared to their size, $D/\sigma < 1$. However, their size can be large or small compared to the mean distance between particles $(V/N)^{1/3}$, depending on whether the density of the system is small or large,

respectively. Most importantly for the purposes here, these forces do not conserve energy. This property captures the feature of real grains that center of mass kinetic energy is lost as they distort during pair collisions. Further details of the force law are not required at this point.

The dynamics consists of straight line motion along the direction of the velocity at time τ (free streaming), until the force range of any pair of particles, say i, j , overlaps. The relative velocity $\mathbf{g}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ of that pair changes according to Newton's second law for the chosen force law $\mathbf{F}_{ij}$. Subsequently, all particles continue to stream freely until another pair has a force range of overlap, and the collisional change is repeated for that pair. In this way a trajectory $\Gamma_t = \{\mathbf{q}_1(t), \dots, \mathbf{q}_N(t), \mathbf{v}_1(t), \dots, \mathbf{v}_N(t)\}$ is generated for $t > 0$. This trajectory is unique and invertible. The statistical mechanics for a fluid of inelastic particles (Brey et al. 1997; Van Noije and Ernst 2001; Dufty et al. 2002; Dufty 2000) is comprised of the dynamics just described, a macrostate specified in terms of a probability density $\rho(\Gamma)$, and a set of observables generically denoted by $A(\Gamma)$. The expectation value for an observable at time $t > 0$ for a state $\rho(\Gamma)$ given at $t = 0$ is defined by

$$\begin{aligned} \langle A(t); 0 \rangle &\equiv \int d\Gamma \rho(\Gamma) A(\Gamma_t) \\ &\equiv \int d\Gamma \rho(\Gamma) e^{tL} A(\Gamma) \end{aligned} \quad (2)$$

where $A(t) = A(\Gamma_t)$, and $\Gamma_t \equiv \{\mathbf{q}_1(t), \dots, \mathbf{q}_N(t), \mathbf{v}_1(t), \dots, \mathbf{v}_N(t)\}$ is the phase point evolved to time t from $\Gamma = \Gamma_{t=0}$. The dynamics can be represented in terms of a generator L defined by the second equality of (2). There are two components to the generator, corresponding to the two steps of free streaming and velocity changes due to interactions

$$\begin{aligned} L = \sum_{i=1}^N \mathbf{v}_i \cdot \nabla_i + \frac{1}{2m} \sum_{i=1}^N \sum_{j \neq i}^N \mathbf{F}_{ij} \\ \cdot (\nabla_{\mathbf{v}_i} - \nabla_{\mathbf{v}_j}). \end{aligned} \quad (3)$$

An alternative equivalent representation of the dynamics is obtained by transferring the dynamics

from the observable $A(\Gamma)$ to the state $\rho(\Gamma)$ by the definition

$$\begin{aligned} \int d\Gamma \rho(\Gamma) e^{tL} A(\Gamma) &\equiv \int d\Gamma \left(e^{-i\bar{L}} \rho(\Gamma) \right) A(\Gamma) \\ &\equiv \int d\Gamma \rho(\Gamma, t) A(\Gamma). \end{aligned} \quad (4)$$

The representation in terms of a dynamical state $\rho(\Gamma, t)$ is referred to as Liouville dynamics. Its generator $\bar{L}$ is the formal adjoint of L which is found to be

$$\bar{L} = L + \frac{1}{2m} \sum_{i=1}^N \sum_{j \neq i}^N (\nabla_{\mathbf{v}_i} - \nabla_{\mathbf{v}_j}) \cdot \mathbf{F}_{ij}. \quad (5)$$

The difference between L and $\bar{L}$ arises because the forces are non-conservative and therefore depend on the relative velocities of each pair as well as their positions. Time correlation functions for two observables A and B are defined in a similar way

$$\begin{aligned} \langle A(t)B; 0 \rangle &\equiv \int d\Gamma (e^{tL} A(\Gamma)) \rho(\Gamma) B(\Gamma) \\ &\equiv \int d\Gamma A(\Gamma) \left(e^{-i\bar{L}} \rho(\Gamma) \right) (e^{-tL} B(\Gamma)). \end{aligned} \quad (6)$$

or

$$\langle A(t)B; 0 \rangle \equiv \langle AB(-t); t \rangle. \quad (7)$$

In summary, averages like $\langle A(t); 0 \rangle$ and correlation functions $\langle A(t)B; 0 \rangle$ are the central properties of interest for a macroscopic description of physical systems. The microscopic dynamics can be represented in terms of the observables $A(\Gamma, t)$ or the states $\rho(\Gamma, t)$ which are determined from specified initial values and the equations

$$(\partial_t - L)A(\Gamma, t) = 0, \quad (\partial_t + \bar{L})\rho(\Gamma, t) = 0. \quad (8)$$

In the following most of the analysis is done in terms of the states, and the associated equation of motion is known as the Liouville equation.

Liouville Equation and Cooling

For an isolated system, the total energy decreases monotonically due to the loss of energy on each pair collision. This is reflected in a decrease of the average kinetic energy of the particles between collisions and hence is referred to as collisional “cooling”. The energy per particle at time t and its loss are

$$\epsilon(t) \equiv N^{-1} \langle E; t \rangle, \quad \omega(t) \equiv -\partial_t \epsilon(t) = N^{-1} \langle LE; t \rangle. \quad (9)$$

This cooling effect is common to all solutions to the Liouville equation and it is useful to separate the dynamics into that due to this cooling and the residual time dependence

$$\rho(\Gamma, t) \equiv \rho(\Gamma, \epsilon(t), t). \quad (10)$$

The Liouville equation then can be written

$$\partial_t \rho(\Gamma, \epsilon, t)|_{\epsilon} + (-\omega(\epsilon, t) \partial_{\epsilon} + \bar{L}) \rho(\Gamma, \epsilon, t) = 0. \quad (11)$$

The time derivative is now taken at constant ϵ . The notation $\omega(\epsilon, t)$ reflects the fact that it is a linear functional of $\rho(\Gamma, \epsilon, t)$, from its definition (9). This is a useful form that isolates a primary effect of the nonconservative forces (cooling) from the residual dynamics that will be associated with relaxation of the spatial inhomogeneities of interest below. For notational simplicity (11) is written

$$(\partial_t + \bar{L}) \rho(\Gamma, \epsilon, t) = 0, \quad \bar{L} \equiv -\omega(\epsilon, t) \partial_{\epsilon} + \bar{L}. \quad (12)$$

The corresponding equation for observables is

$$(\partial_t - L) A(\Gamma, \epsilon, t) = 0, \quad L \equiv -\partial_{\epsilon} \omega(\epsilon, t) + L. \quad (13)$$

where it is understood that ∂_{ϵ} operates on everything to its right.

Stationary Homogeneous State

An isolated normal fluid supports an equilibrium state. This is a stationary solution to the Liouville equation with translational invariance, the Gibbs

states. From the discussion above it is clear that isolated granular fluids have no truly stationary state due to cooling. However, there is a “universal” homogeneous state similar to the Gibbs state in the sense that a wide class of homogeneous initial states rapidly approach this state, on the time scale of a few collisions per particle. It is simple in the sense that all of its time dependence is that associated with cooling

$$\rho_0(\Gamma, t) = \rho_0\left(\left\{\mathbf{q}_{ij}, \mathbf{v}_i\right\}, \epsilon(t)\right). \quad (14)$$

Here, $\mathbf{q}_{ij} = \mathbf{q}_i - \mathbf{q}_j$ so the solution also has translational invariance. In the representation (12) it is seen to be a stationary solution to the Liouville equation

$$\bar{L}\rho_0 = 0. \quad (15)$$

There is no longer any explicit time dependence since $\omega(\epsilon, t) = \omega(\epsilon)$ and $\bar{L} = -\omega(\epsilon) \partial_\epsilon + \bar{L}$ for this state. This solution is referred to as the homogeneous cooling state (HCS). Clearly, it is the close analogue of the Gibbs state for a normal fluid. It is an example of a “normal” state in the sense that all of its time dependence occurs through one of the hydrodynamic fields (the energy). This concept is sharpened below.

Macroscopic Balance Equations

The origins of a macroscopic description for a fluid are the balance equations for the average mass density $\langle m(\mathbf{r}); t \rangle$, energy density $\langle e(\mathbf{r}); t \rangle$, and momentum density $\langle \mathbf{g}(\mathbf{r}); t \rangle$, where $\mathbf{r}$ denotes an arbitrary field point within the system (Dufty and Brey 2005a). These will be referred to as the hydrodynamic fields since they are the ones that are expected to obey the hydrodynamic equations under appropriate conditions. The phase functions $M(\Gamma, \mathbf{r})$, $E(\Gamma, \mathbf{r})$, and $\mathbf{g}(\Gamma, \mathbf{r})$ are well known and their explicit forms will not be needed here. They will be denoted collectively by $A_A(\mathbf{r})$

$$a_\alpha(\mathbf{r}, t) \leftrightarrow \{m(\mathbf{r}), e(\mathbf{r}), \mathbf{g}(\mathbf{r})\}. \quad (16)$$

It follows from (8) that they obey the microscopic balance equations (Dufty et al. 2007)

$$\partial_t a_\alpha(\mathbf{r}, t) = La_\alpha(\mathbf{r}, t) = -\nabla \cdot \mathbf{b}_\alpha(\mathbf{r}, t) - \delta_{\alpha 2} w(\mathbf{r}, t). \quad (17)$$

To obtain this result, it has been recognized that the quantity $-La_A(\mathbf{r}, t)$ can be written as the sum of a divergence $\nabla \cdot \mathbf{b}_\alpha(\mathbf{r}, t)$ plus a remainder $w(\mathbf{r}, t)$ that cannot be so represented. For a normal fluid $w(\mathbf{r}, t)$ vanishes and (17) become the local conservation laws for mass, energy, and momentum. The $\mathbf{b}_\alpha(\mathbf{r}, t)$ are the corresponding fluxes. This clarifies why $A_A(\mathbf{r}, t)$ are selected for a macroscopic description. Their time dependence is determined by the scale of the spatial gradients of the fluxes, and averages of the latter become small as the system approaches homogeneity. Consequently, on long time scales the $\langle a_\alpha(\mathbf{r}); t \rangle$ are the only surviving dynamical variables, and it is under these conditions that these fields obey hydrodynamic equations. The mass and momentum are conserved for a granular fluid as well, but there is a loss of energy $w(\mathbf{r}, t)$ due to the non-conservative forces. It is no longer obvious that the energy is still one of the slow variables since its time scale is coupled to $w(\mathbf{r}, t)$ which does not become small for nearly homogeneous states. Thus, an additional requirement for the existence of a macroscopic description in terms of $\langle a_\alpha(\mathbf{r}); t \rangle$ is that the time scale of $\langle e(\mathbf{r}); t \rangle / \langle w(\mathbf{r}); t \rangle$ must be larger than that for nonhydrodynamic properties. This issue is discussed further below.

The macroscopic balance equations follow from the averages of (17)

$$\begin{aligned} \partial_t \langle a_\alpha(\mathbf{r}); t \rangle + \nabla \cdot \langle \mathbf{b}_\alpha(\mathbf{r}); t \rangle \\ = -\delta_{\alpha 2} \langle w(\mathbf{r}); t \rangle. \end{aligned} \quad (18)$$

These equations are formally exact, but of little practical use as they do not form a closed (self-deterministic) set of equations for $\langle a_\alpha(\mathbf{r}); t \rangle$. Closure requires expressing the average flux $\langle \mathbf{b}_\alpha(\mathbf{r}); t \rangle$ and energy loss $\langle w(\mathbf{r}); t \rangle$ as functionals of the fields $\langle a_\alpha(\mathbf{r}); t \rangle$. Such relationships are called “constitutive equations”. The combination of the exact balance equations with some form of constitutive equations provides the most general definition of hydrodynamics.

Construction of the constitutive equations is simplified by extracting the effects of convection.

The velocity $\mathbf{U}(\mathbf{r}, t)$ of a cell at point $\mathbf{r}$ is defined in terms of the average momentum

$$\langle g(\mathbf{r}); t \rangle \equiv \langle m(\mathbf{r}); t \rangle \mathbf{U}(\mathbf{r}, t). \quad (19)$$

The fluxes are functions of the positions and velocities $\mathbf{b}_\alpha(\mathbf{r}) = \mathbf{b}_\alpha(\mathbf{r}; \{\mathbf{q}_i, \mathbf{v}_i\}) = \mathbf{b}_\alpha(\mathbf{r}; \{\mathbf{q}_i, \mathbf{V}_i + \mathbf{U}(\mathbf{r})\})$, where the velocity in the local rest frame has been introduced, $\mathbf{V}_i = \mathbf{v}_i - \mathbf{U}(\mathbf{r}, t)$. Then defining the microscopic flux in the rest frame by $\mathbf{b}'_\alpha(\mathbf{r}) = \mathbf{b}_\alpha(\mathbf{r}; \{\mathbf{q}_i, \mathbf{V}_i\})$ it follows that the average flux has the form (McLennan 1989).

$$\begin{aligned} \langle \mathbf{b}_\alpha(\mathbf{r}); t \rangle &= \langle \mathbf{b}'_\alpha(\mathbf{r}); t \rangle + \mathbf{c}_{\alpha\eta} \mathbf{U}(\mathbf{r}, t) \cdot \langle \mathbf{b}'_\eta(\mathbf{r}); t \rangle \\ &+ \mathbf{U}(\mathbf{r}, t) d_\alpha(\langle \langle a_\nu(\mathbf{r}); t \rangle \rangle). \end{aligned} \quad (20)$$

The first term is the flux of mass, energy, and momentum in a fluid element at rest, and represents the dissipative processes. The second and third terms are proportional to the flow velocity $\mathbf{U}(\mathbf{r}, t)$ and are associated with convection. The coefficients of these terms are explicit functions of the fields $\langle a_\alpha(\mathbf{r}); t \rangle$ (as is $\mathbf{U}(\mathbf{r}, t)$). For a normal fluid, neglect of the rest frame fluxes leads to the perfect fluid Euler hydrodynamic equations. Hence, determination of the constitutive equations is reduced to expressing the rest frame fluxes and energy loss as functionals of the fields.

“Normal” States and Hydrodynamics

A hydrodynamic description is a closed set of equations for the hydrodynamic fields, $\langle a_\alpha(\mathbf{r}); t \rangle$. This follows from the exact macroscopic balance equations if the energy loss and fluxes can be represented as functionals of these fields

$$\begin{aligned} \langle w(\mathbf{r}); t \rangle &\rightarrow \omega(\mathbf{r} | \langle a_\alpha; t \rangle), \\ \langle \mathbf{b}_\alpha(\mathbf{r}); t \rangle &\rightarrow \beta_\alpha(\mathbf{r} | \langle a_\alpha; t \rangle). \end{aligned} \quad (21)$$

The arrow is used to indicate that such a functional representation need not be valid on all length and time scales, and any such restrictions constitute the domain of validity for hydrodynamics. The notation here and below is such that $f(\mathbf{r}, t, \{\langle a_\alpha(\mathbf{r}); t \rangle\})$ denotes a *function* of $\mathbf{r}, t$ and

of the fields $\langle a_\alpha(\mathbf{r}); t \rangle$ at the point $\mathbf{r}$, while $f(\mathbf{r}, t, | \langle a_\alpha; t \rangle)$ denotes a function of $\mathbf{r}, t$ and a *functional* of the $\langle a_\alpha; t \rangle$ at all space points. With such constitutive relations the macroscopic balance Eqs. (18) become hydrodynamic equations

$$\partial_t \langle a_\alpha(\mathbf{r}); t \rangle + \nabla \cdot \beta(\mathbf{r} | \langle a_\alpha; t \rangle) = -\delta_{\alpha 2} \omega(\mathbf{r} | \langle a_\alpha; t \rangle). \quad (22)$$

The average energy loss and fluxes are averages of specific functions of the particle positions and velocities, and hence are linear functionals of the solution to the Liouville equation. The existence of constitutive equations is therefore related to a special property of the solution which will be called “normal” (this terminology originates in a related context for derivation of hydrodynamics from the Boltzmann kinetic equation (McLennan 1989)). The class of “normal” distributions is defined by the functional forms

$$\rho_n(\Gamma, t) = \rho_n \left(\left\{ \mathbf{q}_{ij}, \mathbf{v}_i \right\} | \langle a_\alpha; t \rangle \right). \quad (23)$$

All time dependence and all the breaking of translational invariance for normal states occurs only through the hydrodynamic fields. A familiar example of a normal distribution for real fluids is the *LOCAL* Gibbs distribution

$$\rho_{el}(\Gamma | \langle a_\alpha; t \rangle) = \exp \left\{ q - \int d\mathbf{r} y_\alpha(\mathbf{r}, t) a_\alpha(\mathbf{r}) \right\}. \quad (24)$$

Here q is a normalization constant, and $y_\alpha(\mathbf{r}, t)$ are conjugate fields determined by the requirement that the averages of $A_\alpha(\mathbf{r})$ give the specified values $\langle a_\alpha(\mathbf{r}); t \rangle$. In this way $y_\alpha(\mathbf{r}, t)$ are functionals of the hydrodynamic fields and $\rho_{el}(\Gamma | \langle a_\alpha; t \rangle)$ is normal. The importance of normal solutions is that they yield directly the desired functionals of (21)

$$\omega(\mathbf{r} | \langle a_\alpha; t \rangle) = \int d\Gamma \rho_n(\Gamma | \langle a_\alpha; t \rangle) w(\mathbf{r}) \quad (25)$$

$$\beta_\alpha(\mathbf{r} | \langle a_\alpha; t \rangle) = \int d\Gamma \rho_n(\Gamma | \langle a_\alpha; t \rangle) \mathbf{b}_\alpha(\mathbf{r}). \quad (26)$$

The normal state in (25) and (26) must be a solution to the Liouville equation. In general, the

time derivative in the Liouville equation can be separated into that which occurs through $\langle a_\alpha; t \rangle$ plus the residual time dependence, generalizing (10)

$$\rho(\Gamma, t) = \rho(\Gamma, t | \langle a_\alpha; t \rangle). \quad (27)$$

The Liouville equation then becomes

$$\begin{aligned} \partial_t \rho |_{\langle a_\alpha; t \rangle} - \int d\mathbf{r} \frac{\delta \rho}{\delta \langle a_\alpha(\mathbf{r}); t \rangle} \\ \cdot \{ \nabla \cdot \langle \mathbf{b}_\alpha(\mathbf{r}); t \rangle + \delta_{\alpha 2} \langle w(\mathbf{r}); t \rangle \} + \bar{L} \rho = 0. \end{aligned} \quad (28)$$

A normal solution results when $\partial_t \rho_n |_{\langle a_\alpha; t \rangle} \rightarrow 0$. For specified fields, (28) becomes an equation for the Γ dependence of the normal phase space density as a functional of the fields. This dependence then allows determination of the normal forms in (25) and (26). Finally, with the form of the hydrodynamic equation determined at that point, their solution with suitable initial and boundary conditions provides the explicit forms for the fields, and completes the normal solution. The existence and determination of this solution is the central problem for establishing a hydrodynamic description for both normal and granular fluids.

The concept of a normal solution and its use in the macroscopic balance equations makes no special reference to whether the fluid is atomic or granular, and is not restricted to states near homogeneity. In this general context, hydrodynamics is not a simple set of local partial differential equations such as the familiar Navier–Stokes equations. The latter are a special case of this more general idea, and their inadequacy for some conditions should not be interpreted as the absence of a more complex hydrodynamic description.

In closing this Section a qualitative explanation of why a normal solution can be expected is given, by analogy with the similar expectation for atomic fluids. For a wide class of initial states there is a first stage of rapid velocity relaxation in each small region toward the universal homogeneous state (HCS or Gibbs, respectively). However, the hydrodynamic parameters of that universal state are specific

to each region so it is only locally homogenous, as in (24) for the atomic fluid. Subsequently, these differences in the parameters of neighboring cells are decreased by the fluxes of mass, energy, and momentum across their boundaries. It is this second stage where a normal description in terms of the hydrodynamic fields can be expected, indicating also that the space and time scales for a hydrodynamic description should be large compared to those of the first stage. This basic conceptual picture is essentially the same for both atomic and granular fluids, and the rapid approach of the first stage is indeed observed in molecular dynamics simulation studies of both equilibrium and the HCS.

Navier–Stokes Approximation

Equation (28) presents a formidable problem and further progress requires specialization to specific cases of interest. Perhaps the simplest of these are weakly inhomogeneous states. These are states for which all spatial gradients of first order are small and all higher order derivatives are negligible. Small gradients means that the relative change in the hydrodynamic fields over the largest microscopic length scale ℓ_0 is small: $\ell_0 \partial_r \ln \langle a_\alpha; t \rangle \ll 1$. There are two characteristic length scales, the mean free path and the grain diameter. For a dilute gas the mean free path is largest, while for a dense fluid the grain size is largest. Under these conditions a solution to the Liouville equation can be sought as an expansion to leading order in these small gradients. This will be referred to as the Navier–Stokes approximation.

According to the discussion at the end of the last section, a normal solution is expected after the system has relaxed to its local HCS form, denoted by $\rho_{0\ell}(\Gamma | \langle a_\alpha; t \rangle)$, representing the fluid as having each cell in its own HCS. Define the deviations of the hydrodynamic fields from some common reference value by

$$\delta \langle a_\alpha; t \rangle = \langle a_\alpha; t \rangle - a_{0\alpha}, \quad (29)$$

where $a_{0\alpha}$ is the same for all cells. Then, the local HCS must satisfy the conditions

$$\rho_{0\ell}(\Gamma|a_{0z} + \delta\langle a_z; t \rangle)|_{\delta\langle a_z; t \rangle=0} = \rho_0(\Gamma; a_{0z}), \quad (30)$$

$$\begin{aligned} & \frac{\partial \rho_0}{\partial a_{0z}} \\ &= \int d\mathbf{r} \frac{\delta \rho_{0\ell}(\Gamma|a_{0z} + \delta\langle a_z; t \rangle)}{\delta \langle a_z(\mathbf{r}); t \rangle} \Big|_{\delta\langle a_z; t \rangle=0}, \dots \end{aligned} \quad (31)$$

i.e., the local HCS and all of its functional derivatives must agree with those of the HCS in the homogenous limit. Also, as a normal distribution its time dependence is through the exact hydrodynamic fields for the fluid state considered. This means the averages of the corresponding microscopic fields $A_A(\mathbf{r})$ for the local HCS and for the solution to the Liouville equation must be the same

$$\int d\Gamma (\rho - \rho_{0\ell}) a_z(\mathbf{r}) = 0. \quad (32)$$

A more complete discussion of the construction of $\rho_{0\ell}$ from knowledge of ρ_0 is given elsewhere (Dufty et al. 2007). For the purposes here properties (30), (31), and (32) are sufficient.

The local HCS distribution, $\rho_{0\ell}$, is not a solution to the Liouville equation except in limit that all hydrodynamic fields become the same for each cell. Instead, it is a reference state approximating the actual solution after its first stage of velocity relaxation. To construct a solution p define its deviation from $\rho_{0\ell}$ by

$$\rho(\Gamma, t|\langle a_z; t \rangle) = \rho_{0\ell}(\Gamma, t|\langle a_z; t \rangle) + \Delta(\Gamma, t|\langle a_z; t \rangle). \quad (33)$$

The Liouville Equation (28) gives

$$\begin{aligned} & \partial_t \Delta - \int d\mathbf{r}' \frac{\delta \Delta}{\delta \langle a_z(\mathbf{r}'); t \rangle} \\ & \quad \cdot \{\nabla \cdot \langle \mathbf{b}_x(\mathbf{r}); t \rangle + \delta_{x2} \langle w(\mathbf{r}); t \rangle\} + \bar{L} \Delta \\ &= \int d\mathbf{r}' \frac{\delta \rho_{0\ell}}{\delta \langle a_z(\mathbf{r}'); t \rangle} \\ & \quad \cdot \{\nabla \cdot \langle \mathbf{b}_x(\mathbf{r}); t \rangle + \delta_{x2} \langle w(\mathbf{r}); t \rangle\} - \bar{L} \rho_{0\ell}. \end{aligned} \quad (34)$$

This equation is still exact, but if only small gradient states are considered it simplifies by retaining terms only of first order in the gradients.

To be precise, the ultimate use of this solution is to calculate local properties of the form

$$\begin{aligned} & A(\mathbf{r}, t|\{y_\alpha(t)\}) \\ &= \int d\Gamma a(\Gamma, \mathbf{r}) \rho(\Gamma, t|\langle a_z(\mathbf{r}); t \rangle + \delta\langle a_z; t \rangle). \end{aligned} \quad (35)$$

Therefore, in the following analysis the gradient expansions are referred to the field point $\mathbf{r}$ of interest, $\langle a_\alpha; t \rangle = \langle a_\alpha(\mathbf{r}); t \rangle + \delta\langle a_\alpha; t \rangle$, i.e. the common reference values in (29) are the exact field values at the chosen point, $a_{0\alpha} = \langle a_\alpha(\mathbf{r}); t \rangle$. The gradient expansion is carried out relative to these values. Of course the results will be general and applicable to any choice for $\mathbf{r}$.

The details of the gradient expansion are given in the Appendix. The solution to the Liouville equation to first order in the gradients is

$$\begin{aligned} \rho(\Gamma, t|\langle a_z; t \rangle) &= \rho_0(\Gamma, \langle a_z(\mathbf{r}); t \rangle) + (1 - \mathcal{P}) \\ & \quad \cdot \left(\mathbf{M}_\beta(\Gamma, \langle a_z(\mathbf{r}); t \rangle) + \int_0^t d\Gamma' \left(e^{-(I\bar{L} + K^T)\Gamma'} \right)_{\beta\nu} \right. \\ & \quad \cdot (1 - \mathcal{P}) \mathbf{Y}_\nu(\Gamma, \langle a_z(\mathbf{r}); t \rangle) \left. \right) \cdot \nabla \langle a_\beta(\mathbf{r}); t \rangle. \end{aligned} \quad (36)$$

with the definitions

$$\mathbf{M}_\beta = \int d\mathbf{r}' \left(\frac{\delta \rho_{0\ell}}{\delta \langle a_z(\mathbf{r}'); t \rangle} \right)_{\delta\langle a_z; t \rangle=0} \mathbf{r}', \quad (37)$$

$$\mathbf{Y}_\alpha = -(I\bar{L} + K^T)_{\alpha\beta} \mathbf{M}_\beta. \quad (38)$$

The generator for the dynamics $I\bar{L} + K^T$ has a contribution from $\bar{L}$ which is the same as in (12), with ω evaluated for the HCS as a function of the exact hydrodynamic fields at the point $\mathbf{r}$ and time t .

$$\bar{L} = -\omega_0(\langle a_z(\mathbf{r}); t \rangle) \partial_{\langle a_z(\mathbf{r}); t \rangle} + \bar{L}. \quad (39)$$

The second contribution to the generator of the dynamics is the transpose of the matrix K_{AB}

$$K_{\alpha\beta} = \delta_{\alpha 2} \frac{\partial \omega_0(\langle a_z(\mathbf{r}); t \rangle)}{\partial \langle a_\beta(\mathbf{r}); t \rangle}. \quad (40)$$

Finally, $\mathcal{P}$ is a projection operator

$$\begin{aligned}
\mathcal{P}X &= \Psi_\beta \int d\Gamma A_\beta X, \\
A_\beta &= V^{-1} \int d\mathbf{r} a_\beta(\mathbf{r}), \\
\Psi_\beta &\equiv \frac{\partial \rho_0}{\partial \langle a_\beta(\mathbf{r}); t \rangle}
\end{aligned} \quad (41)$$

The phase functions A_β and Ψ_β form a biorthogonal set in the sense

$$\int d\Gamma A_\alpha \Psi_\beta = \delta_{\alpha\beta}. \quad (42)$$

The A_α are the usual global invariants of the Liouville operator $\bar{L}$ for a normal fluid; it is shown in the Appendix that the Ψ_β are the invariants of the new generator for dynamics in a granular fluid

$$(\bar{L}_T + K^T)_{\nu\beta} \Psi_\beta = 0. \quad (43)$$

Equation (36) is not quite the normal solution desired. All terms depend on time through $\langle a_\beta(\mathbf{r}); t \rangle$ as required, except for the last term which has an additional explicit time dependence through the upper limit of the time integral. This time dependence becomes negligible if the integrand is effectively non-zero after some short time scale τ . Then for $t \gg \tau$ the time integral becomes independent of t and can be taken formally to infinity. Thus, a normal solution is attained for this time scale

$$\begin{aligned}
\rho_n(\Gamma, \langle a_\alpha(\mathbf{r}); t \rangle) &= \rho_0(\Gamma, \langle a_\alpha(\mathbf{r}); t \rangle) \\
&+ (1 - \mathcal{P})(\mathbf{M}_\beta(\Gamma, \langle a_\alpha(\mathbf{r}); t \rangle)) \\
&+ \lim_{t_0 \rightarrow \infty} \int_0^{t_0} dt' \left(e^{-(\bar{L}_T + K^T)t'} \right)_{\beta\nu} \\
&\cdot (1 - \mathcal{P}) \mathbf{Y}_\nu(\Gamma, \langle a_\alpha(\mathbf{r}); t \rangle) \\
&\cdot \nabla \langle a_\beta(\mathbf{r}); t \rangle.
\end{aligned} \quad (44)$$

It is expected that the integrand should have this property of a short time scale since the domain of operation for the generator of time dependence is functions with translational invariance (as a consequence of the gradient expansion). Hence

there are no explicit slow hydrodynamic modes of finite wavelength. Also, there is no contribution from the homogeneous hydrodynamics (that for the invariants) due to the orthogonal projection $(1 - \mathcal{P})$. The appearance of this projection is an essential self-consistency of the analysis, and occurs as well for normal fluids. The expression (44) is only formal and the actual limit should be taken in the weak sense only after (36) has been used to define average properties. A technical complication is the occurrence of periodic time dependence, the Poincare recurrence time. This can be removed by considering the thermodynamic limit of $V \rightarrow \infty$, $N \rightarrow \infty$ at constant N/V . Therefore, averages using the normal solution to the Liouville equation are understood as having the thermodynamic limit followed by the long time limit at constant $\langle a_\alpha(\mathbf{r}); t \rangle$.

An alternative equivalent form results from performing the integral in (44) using the explicit form (38) and the property (99) of the Appendix

$$\begin{aligned}
\rho_n(\Gamma, \langle a_\alpha(\mathbf{r}); t \rangle) &= \rho_0(\Gamma, \langle a_\alpha(\mathbf{r}); t \rangle) \\
&+ \lim_{t_0 \rightarrow \infty} (1 - \mathcal{P}) \left(e^{-(\bar{L}_T + K^T)t_0} \right)_{\beta\nu} \\
&\cdot \mathbf{M}_\nu(\Gamma, \langle a_\alpha(\mathbf{r}); t \rangle) \cdot \nabla \langle a_\beta(\mathbf{r}); t \rangle.
\end{aligned} \quad (45)$$

The decay time for the integrand of (44) now becomes the time after which (45) reaches its normal form.

Constitutive Equations

The exact macroscopic balance equations are given by (22), and the necessary constitutive equations are given by (26) and (27) as averages over the normal solution. These can be made more explicit now using the small gradient result (44). Since the latter is a local function of the fields, the constitutive equations also will be local. Furthermore, since all components of the gradients in (45) depend on the common value $\langle \mathbf{g}(\mathbf{r}); t \rangle$, this can be eliminated through a Galilean transformation so that all properties refer to a fluid element at rest. Of course, the gradients of $\langle \mathbf{g}(\mathbf{r}); t \rangle$ in that fluid element are nonzero.

Consider first the energy loss function ω

$$\begin{aligned}\omega(\langle a_x(\mathbf{r}); t \rangle) &= \int d\Gamma \rho_n(\Gamma, \langle a_x(\mathbf{r}); t \rangle) w(\mathbf{r}) \\ &= \int d\Gamma \rho_n(\Gamma, \langle a_x(\mathbf{r}); t \rangle) \bar{w}.\end{aligned}\quad (46)$$

The coefficients of the gradient in the normal solution have translational invariance and the average is independent of $\mathbf{r}$, except through its parametrization by $\langle a_x(\mathbf{r}); t \rangle$. The second equality takes this into account by replacing $w(\mathbf{r})$ by its average $\bar{w}$

$$\bar{w} = V^{-1} \int d\mathbf{r} w(\mathbf{r}). \quad (47)$$

Since $\omega(\langle a_x(\mathbf{r}); t \rangle)$ is a scalar, fluid symmetry restricts the contributions to first order in the gradients to

$$\begin{aligned}\omega(\langle a_x(\mathbf{r}); t \rangle) &= \omega_0(\langle a_x(\mathbf{r}); t \rangle) + \omega_1(\langle a_x(\mathbf{r}); t \rangle) \nabla \cdot \mathbf{U}(\mathbf{r}, t).\end{aligned}\quad (48)$$

Here, the flow velocity $\mathbf{U}(\mathbf{r}, t)$ of (19) has been used in place of the momentum density. The first term is the contribution from the HCS distribution

$$\omega_0(\langle a_x(\mathbf{r}); t \rangle) = \int d\Gamma \rho_0(\Gamma, \langle a_x(\mathbf{r}); t \rangle) \bar{w}. \quad (49)$$

The coefficient of $\nabla \cdot \mathbf{U}(\mathbf{r}, t)$ is

$$\begin{aligned}\omega_1(\langle a_x(\mathbf{r}); t \rangle) &= \lim_{t_0 \rightarrow \infty} C_\omega(t_0, \langle a_x(\mathbf{r}); t \rangle) \\ &= C_\omega(0, \langle a_x(\mathbf{r}); t \rangle) \\ &\quad + \lim_{t_0 \rightarrow \infty} \int_0^{t_0} \partial_{t'} C_\omega(t', \langle a_x(\mathbf{r}); t \rangle) dt'\end{aligned}\quad (50)$$

with the correlation function defined by

$$C_\omega(t) = \int d\Gamma \bar{w} (1 - \mathcal{P}) e^{-\bar{L}t} M_U, \quad (51)$$

$$M_U \equiv \frac{1}{3} \int d\mathbf{r}' \mathbf{r}' \cdot \left(\frac{\delta \rho_{0\ell}}{\delta \mathbf{U}(\mathbf{r}', t)} \right)_{\delta \langle a_x; t \rangle = 0}. \quad (52)$$

The coefficient ω_0 defines an “equation of state” for the granular hydrodynamics, and gives the first non-trivial result of this analysis. It is similar to the pressure (given below) and is an inherent property of the local state of each cell, independent of the gradients between cells. In contrast, ω_1 is a true transport coefficient characterizing communication between cells. The first equality of (50) provides the Helfand form for this coefficient, while the second equality gives the equivalent Green–Kubo form. Each has its practical utility, depending on the method used for its approximate evaluation. Both forms have proven useful for normal fluids, and further discussion is provided below. Both ω_0 and the transport coefficient ω_1 vanish for normal fluids since they characterize collisional energy loss.

The fluxes β_α of (26) can be determined in a similar way. As indicated in (20), only the rest frame flux β'_x is required. Furthermore, since all components of the gradients in (45) depend on the common value $\langle \mathbf{g}(\mathbf{r}); t \rangle$, this can be eliminated through a Galilean transformation so that all properties refer to a fluid element at rest. Of course, the gradients of $\langle \mathbf{g}(\mathbf{r}); t \rangle$ in that fluid element are nonzero. The component β'_1 is the rest frame mass flux which is expected to vanish in order to give the continuity equation. This follows from the fact that $\mathbf{b}'_1(\mathbf{r})$ is the microscopic momentum density

$$\begin{aligned}\beta'_1 &= \int d\Gamma \mathbf{g}(\mathbf{r}) \rho_0(\Gamma, \langle a_x(\mathbf{r}); t \rangle) \\ &\quad + \lim_{t_0 \rightarrow \infty} \int d\Gamma \mathbf{g}(\mathbf{r}) (1 - \mathcal{P}) (\dots) = 0\end{aligned}\quad (53)$$

The first term vanishes since $\langle \mathbf{g}(\mathbf{r}); t \rangle = 0$ in the rest frame, and the second term vanishes since $(1 - \mathcal{P})$ projects orthogonal to the mass, energy, and momentum. Thus, the expected continuity equation is verified.

The fluxes β'_2 and β'_x for $A = 3, 4, 5$ are the rest frame energy and momentum fluxes. The energy flux transforms like a vector and therefore fluid symmetry (translational and rotational invariance)

requires that it can depend only on gradients of scalars

$$\begin{aligned} \boldsymbol{\beta}'_2 = & -\lambda(\langle a_\alpha(\mathbf{r}); t \rangle) \nabla T(\mathbf{r}, t) \\ & -\mu(\langle a_\alpha(\mathbf{r}); t \rangle) \nabla \langle m(\mathbf{r}); t \rangle. \end{aligned} \quad (54)$$

To make the connection with Fourier's law for an atomic fluid, a temperature $T(\mathbf{r}, t)$ has been introduced through the definition

$$\langle e(\mathbf{r}); t \rangle \equiv e_0(\langle m(\mathbf{r}); t \rangle, T(\mathbf{r}, t)). \quad (55)$$

For an atomic fluid the function $e_0(\langle m(\mathbf{r}); t \rangle, T(\mathbf{r}, t))$ is chosen to be the thermodynamic internal energy density. As there is no thermodynamics for a granular fluid this function is arbitrary and simply constitutes a change of variables from $\langle e(\mathbf{r}); t \rangle$, $\langle m(\mathbf{r}); t \rangle$ to $T(\mathbf{r}, t)$, $\langle m(\mathbf{r}); t \rangle$. In this form (54) is a generalization of Fourier's law where λ is the thermal conductivity (Dufty 2007). The contribution from the gradient of the mass density is new to granular fluids ($\mu = 0$ for atomic fluids). These coefficients are given by

$$\begin{aligned} \lambda(\langle a_\alpha(\mathbf{r}); t \rangle) &= \lim_{t_0 \rightarrow \infty} C_\lambda(t_0, \langle a_\alpha(\mathbf{r}); t \rangle) \\ &= C_\lambda(0, \langle a_\alpha(\mathbf{r}); t \rangle) \\ &\quad + \lim_{t_0 \rightarrow \infty} \int_0^{t_0} \partial_{t'} C_\lambda(t', \langle a_\alpha(\mathbf{r}); t \rangle) dt' \\ \mu(\langle a_\alpha(\mathbf{r}); t \rangle) &= \lim_{t_0 \rightarrow \infty} C_\mu(t_0, \langle a_\alpha(\mathbf{r}); t \rangle) \\ &= C_\mu(0, \langle a_\alpha(\mathbf{r}); t \rangle) \\ &\quad + \lim_{t_0 \rightarrow \infty} \int_0^{t_0} \partial_{t'} C_\mu(t', \langle a_\alpha(\mathbf{r}); t \rangle) dt' \end{aligned} \quad (56)$$

(57)

with the correlation functions

$$\begin{aligned} C_\lambda(t) &= \frac{1}{3} \int d\Gamma \boldsymbol{\beta}'_2 \cdot (1 - \mathcal{P}) e^{-(\bar{\mathcal{L}} + K_{22})t} \mathbf{M}_T, \quad (58) \\ C_\mu(t) &= \frac{1}{3} \int d\Gamma \boldsymbol{\beta}'_2 \cdot (1 - \mathcal{P}) \left(e^{-\bar{\mathcal{L}}t} \left(\mathbf{M}_m + \frac{K_{21}}{K_{22}} \mathbf{M}_T \right) \right. \\ &\quad \left. + e^{-(\bar{\mathcal{L}} + K_{22})t} \left(\frac{\partial e_0}{\partial \langle m(\mathbf{r}); t \rangle} - \frac{K_{21}}{K_{22}} \right) \frac{\partial T}{\partial e_0} \Big|_{\langle m(\mathbf{r}); t \rangle} \mathbf{M}_T \right), \end{aligned} \quad (59)$$

$$\mathbf{M}_T \equiv \int d\mathbf{r}' \mathbf{r}' \left(\frac{\delta \rho_{0\ell}}{\delta T(\mathbf{r}', t)} \right)_{\delta \langle a_\alpha; t \rangle = 0}. \quad (60)$$

$$\mathbf{M}_m \equiv \int d\mathbf{r}' \mathbf{r}' \left(\frac{\delta \rho_{0\ell}}{\delta \langle m(\mathbf{r}'); t \rangle} \right)_{\delta \langle a_\alpha; t \rangle = 0}. \quad (61)$$

Finally, the set of vectors $\boldsymbol{\beta}'_\alpha$ for $\alpha = 3, 4, 5$ define the pressure tensor $\boldsymbol{\beta}'_\alpha \Leftrightarrow P_{ij}$. Fluid symmetry then determines that it can couple only to the momentum gradients, or equivalently the flow velocity gradients, in the form

$$\begin{aligned} P_{ij} &= p(\langle a_\alpha(\mathbf{r}); t \rangle) \delta_{ij} - \eta(\langle a_\alpha(\mathbf{r}); t \rangle) \\ &\quad \cdot \left(\partial_i U_j(\mathbf{r}, t) + \partial_j U_i(\mathbf{r}, t) - \frac{2}{3} \delta_{ij} \nabla \cdot \mathbf{U}(\mathbf{r}, t) \right) \\ &\quad - \kappa(\langle a_\alpha(\mathbf{r}); t \rangle) \delta_{ij} \nabla \cdot \mathbf{U}(\mathbf{r}, t). \end{aligned} \quad (62)$$

The scalar function $p(\langle a_\alpha(\mathbf{r}); t \rangle)$ is the pressure, now identified as

$$p(\langle a_\alpha(\mathbf{r}); t \rangle) = \int d\Gamma \rho_0(\Gamma, \langle a_\alpha(\mathbf{r}); t \rangle) \beta'_{3x}. \quad (63)$$

The transport coefficients in (62) are the shear viscosity $\eta(\langle a_\alpha(\mathbf{r}); t \rangle)$ and the bulk viscosity $\kappa(\langle a_\alpha(\mathbf{r}); t \rangle)$ given by

$$\begin{aligned} \eta(\langle a_\alpha(\mathbf{r}); t \rangle) &= \lim_{t_0 \rightarrow \infty} C_\eta(t_0, \langle a_\alpha(\mathbf{r}); t \rangle) \\ &= C_\eta(0, \langle a_\alpha(\mathbf{r}); t \rangle) \\ &\quad + \lim_{t_0 \rightarrow \infty} \int_0^{t_0} \partial_{t'} C_\eta(t', \langle a_\alpha(\mathbf{r}); t \rangle) dt' \end{aligned} \quad (64)$$

$$\begin{aligned} \kappa(\langle a_\alpha(\mathbf{r}); t \rangle) &= \lim_{t_0 \rightarrow \infty} C_\kappa(t_0, \langle a_\alpha(\mathbf{r}); t \rangle) \\ &= C_\kappa(0, \langle a_\alpha(\mathbf{r}); t \rangle) \\ &\quad + \lim_{t_0 \rightarrow \infty} \int_0^{t_0} \partial_{t'} C_\kappa(t', \langle a_\alpha(\mathbf{r}); t \rangle) dt' \end{aligned} \quad (65)$$

with the correlation functions

$$C_\eta(t) = \int d\Gamma \beta'_{3y} \cdot (1 - \mathcal{P}) e^{-\bar{\mathcal{L}}t} M_\eta, \quad (66)$$

$$C_\kappa(t) = \int d\Gamma \beta'_{3x} \cdot (1 - \mathcal{P}) e^{-\bar{\mathcal{L}}t} M_\kappa, \quad (67)$$

$$M_\eta \equiv \int d\mathbf{r}' y' \left(\frac{\delta \rho_{0\ell}}{\delta U_y(\mathbf{r}', t)} \right)_{\delta \langle a_x; t \rangle = 0}. \quad (68)$$

$$M_\kappa \equiv \int d\mathbf{r}' y' \left(\frac{\delta \rho_{0\ell}}{\delta U_y(\mathbf{r}', t)} \right)_{\delta \langle a_x; t \rangle = 0}. \quad (69)$$

This completes the formal derivation of the constitutive equations leading to the nonlinear Navier–Stokes equations, including expressions for the cooling rate, energy flux, and pressure tensor including contributions up through first order in the gradients of the hydrodynamic fields. These expressions are functions of the hydrodynamic fields to be determined by their detailed many-body analysis of the correlation functions.

Green–Kubo Expressions

To contrast the results here with those for an atomic fluid, it is instructive to focus on the Green–Kubo forms for the transport coefficients (McLennan 1989). These are given by the second equalities of (50), (56), (57), (64), and (65); the first equalities are the corresponding Helfand forms (Helfand 1960). For atomic fluids there is no counter part to ω_1 and μ . However, there are Green–Kubo expressions for the thermal conductivity and the two viscosities. For the discussion here only the thermal conductivity is considered, whose Green–Kubo expression is

$$\begin{aligned} \lambda(\langle a_x(\mathbf{r}); t \rangle) &= C_\lambda(0, \langle a_x(\mathbf{r}); t \rangle) \\ &+ \lim_{t_0 \rightarrow \infty} \int_0^{t_0} \partial_{t'} C_\lambda(t', \langle a_x(\mathbf{r}); t \rangle) dt' \end{aligned} \quad (70)$$

$$\begin{aligned} \partial_t C_\lambda(t) &= \frac{1}{3} \int d\Gamma \beta'_2 \\ &\cdot (1 - \mathcal{P}) e^{-(\bar{\mathcal{L}} + K_{22})t} \mathbf{Y}_\lambda, \end{aligned} \quad (71)$$

$$\mathbf{Y}_e = -(\bar{\mathcal{L}} + K_{22}) \mathbf{M}_e. \quad (72)$$

In contrast the thermal conductivity for an atomic fluid is

$$\lambda(\langle a_x(\mathbf{r}); t \rangle) \rightarrow \lim_{t_0 \rightarrow \infty} \int_0^{t_0} \partial_{t'} C_\lambda(t', \langle a_x(\mathbf{r}); t \rangle) dt' \quad (73)$$

$$\begin{aligned} \partial_t C_\lambda(t) &\rightarrow \frac{1}{3T^2} \int d\Gamma \beta'_2 \\ &\cdot (1 - \mathcal{P}) e^{-Lt} \beta'_2 \rho_e, \end{aligned} \quad (74)$$

In this last expression ρ_e is the equilibrium Gibbs ensemble, and it is understood that β'_2 is the microscopic expression for the energy flux for a dynamics with conservative forces, and L is the Liouville generator for the corresponding dynamics.

There are several similarities and differences between the granular and atomic fluid expressions (Dufty et al. 2007). The latter is the time integral of a energy flux – energy flux equilibrium time correlation function. The granular fluid is similar, with one of the fluxes the same but the other flux is generated from the local HCS state. Also, the generator for the dynamics in the granular case has two additional effects, L replaced by $\bar{\mathcal{L}} + K_{22}$, to represents homogeneous cooling of the reference state and its homogeneous response to perturbations. The projection orthogonal to the invariants of each dynamics $(1 - \mathcal{P})$ occurs in both cases as a necessary condition for the long time limit of the time integral, and the corresponding existence of the normal state. Finally, the contribution from $C_\lambda(0, \langle a_x(\mathbf{r}); t \rangle)$ vanishes for a normal fluid (except for singular forces) but is non-zero for the granular fluid due to the non-conservative forces.

Navier–Stokes Hydrodynamic Equations

In closing this section it is appropriate to record the results of substituting the Navier–Stokes constitutive equations, valid to first order in the gradients, into the exact macroscopic balance equations. This defines the Navier–Stokes hydrodynamic equations for a granular fluid

$$D_t m + m \nabla_{\mathbf{r}} \cdot \mathbf{U} = 0 \quad (75)$$

$$D_t e_0 + \omega_0 + \left(p + \omega_1 + \left(\frac{2}{3} \eta - \kappa \right) \nabla \cdot \mathbf{U} \right) \nabla \cdot \mathbf{U} - \eta (\partial_\alpha U_\beta + \partial_\beta U_\alpha) \partial_\alpha U_\beta - \nabla \cdot (\lambda \nabla T + \mu \nabla m) = 0, \quad (76)$$

$$D_t U_\alpha + m^{-1} \partial_\alpha \left(p - \left(\frac{2}{3} \eta + \kappa \right) \nabla \cdot \mathbf{U} \right) - m^{-1} \partial_\beta \eta (\partial_\alpha U_\beta + \partial_\beta U_\alpha) = 0. \quad (77)$$

For simplicity of notation, $m \equiv \langle m(\mathbf{r}); t \rangle$ in these equations. They are a set of five nonlinear partial differential equations for the variables M , E_0 , and $\mathbf{U}$. They are a closed set of equations since ω_0 , p , and the transport coefficients ω_1 , λ , μ , η , and κ are defined as functions of these variables. These definitions for the constitutive equations are the primary accomplishment of the statistical mechanical basis for the hydrodynamic equations. The form of (64)–(65) could have been guessed from the outset based on the macroscopic balance equations and fluid symmetry. The underlying basis in the microdynamics of the particles provides the necessary details for how the parameters of these equations must depend on the fields. Here only the formal definitions have been identified. It is only the first half of the problem of completing these equations, as the evaluation of these definitions poses a difficult many body problem. Still, without this first half, the starting point for that detailed analysis would not be possible. This the case for atomic fluids as well.

Future Directions

The objective here has been to formulate the basis for a macroscopic description of granular fluids using the fundamental principles of non-equilibrium statistical mechanics. The analysis presented follows that for an atomic fluid. First, the exact macroscopic balance equations are identified. Next, their closure is linked to the concept of a normal state and corresponding normal

solution to the Liouville equation. This defines the domain of hydrodynamics in its most general sense, both for atomic and granular fluids. The construction of a normal solution is quite difficult in general, but can be accomplished for states with small gradients relative to locally homogeneous conditions. This gives the Navier–Stokes approximation described here.

Navier–Stokes hydrodynamics is applicable for most common states of atomic fluids, while deviations occur primarily for more complex polymeric molecular fluids. The latter have rheological properties corresponding to larger gradients relative to additional microscopic length and time scales. The construction of normal states in these cases is more difficult and is still at the semi-phenomenological stage (Bird et al. 1977). Granular fluids provide a new motivation for renewed efforts to describe these more complex normal states. The reason is that even structurally simple granular fluids composed of spherically symmetric particles can exhibit rheology and other phenomena beyond the Navier–Stokes domain of validity (Santos et al. 2004; Hrenya 2007). This is due to the cooling rate in the energy balance equation which provides a new internal time scale, that can set the size of hydrodynamic gradients beyond any control through boundary conditions. For example, new steady states are possible for granular fluids due to the balance of this internal cooling with external forcing. In many cases this implies that the hydrodynamic description required is beyond the Navier–Stokes domain. The understanding of constitutive equations in these cases is poor at this point. It is hoped that the formal structure described here will provide the appropriate basis for studies of these problems.

The context of hydrodynamics depends on the formation of a normal state from more complex conditions. Above this has been described qualitatively as a two stage process of rapid velocity relaxation in each cell to a state near the local HCS, followed by hydrodynamic relaxation through exchange of mass, energy, and momentum between the cells on a longer time scale. This

separation of microscopic and hydrodynamic time scales is essential to the dominance of the hydrodynamic excitations over all others at large space and time scales. It is justified for atomic fluids since the hydrodynamic times are determined by the wavelength of the phenomena studied. As the system approaches homogeneity, these time scales become much larger than the microscopic excitations and hydrodynamics prevails at large times. However, there is an additional hydrodynamic time scale for granular fluids, the cooling rate, which is not set by the wavelength alone. It would seem that this additional time scale must be large as well, implying a weak cooling rate. This condition is too strong. What matters is the rate of the approach to the homogeneous state, not any dynamics of that final state. In the above derivation of hydrodynamics the final form for the solution to the Liouville equation, Eq. (44) or (45), has a dynamics generated by $I\bar{L} + K^T$ rather than simply that for the trajectories $\bar{L}$. This is significant since the former has the additional compensation for the cooling and for the homogeneous perturbations of that cooling. Hence the approach to the time dependent normal state is determined only by the remaining non-hydrodynamic relaxation. The time scale for relaxation to the normal state is independent of the hydrodynamic time scales of that normal state. Quantitative verification of these concepts is another important future direction for research on a hydrodynamic description for granular fluids.

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Appendix

Gradient expansion In this Appendix the Liouville equation in the form (34) is written to first order in the gradients and solved. Also the invariants of the associated dynamics are identified.

Consider first the right side of (34) which can be written equivalently as

$$\begin{aligned}
 & \int d\mathbf{r}' \frac{\delta\rho_{0\ell}}{\delta\langle a_z(\mathbf{r}'); t \rangle} \left\{ \nabla \cdot \langle \mathbf{b}_z(\mathbf{r}); t \rangle \right. \\
 & \quad \left. + \delta_{z2} \langle w(\mathbf{r}); t \rangle \right\} - \bar{L}\rho_{0\ell} \\
 & = - \int d\mathbf{r}' \frac{\delta\rho_{0\ell}}{\delta\langle a_z(\mathbf{r}'); t \rangle} \langle La_z(\mathbf{r}'); t \rangle - \bar{L}\rho_{0\ell} \\
 & = \int d\mathbf{r}' \frac{\delta\rho_{0\ell}}{\delta\langle a_z(\mathbf{r}'); t \rangle} \int d\Gamma a_z(\mathbf{r}) \bar{L}(\rho_{0\ell} + \Delta) \\
 & \quad - \bar{L}\rho_{0\ell}.
 \end{aligned} \tag{78}$$

The first equality follows from (17) and (21). The first two terms are determined by the local HCS which can be expanded to first order in the gradients

$$\begin{aligned}
 \rho_{0\ell} & = \rho_0(\langle a_z(\mathbf{r}); t \rangle) \\
 & + \int d\mathbf{r}' \left(\frac{\delta\rho_{0\ell}}{\delta\langle a_z(\mathbf{r}'); t \rangle} \right)_{\delta\langle a_z; t \rangle=0} \\
 & \quad \cdot (\langle a_z(\mathbf{r}'); t \rangle - \langle a_z(\mathbf{r}); t \rangle) + \dots \\
 & = \rho_0(\langle a_z(\mathbf{r}); t \rangle) \\
 & + \mathbf{m}_\beta(\mathbf{r}, \langle a_z(\mathbf{r}); t \rangle) \cdot \nabla \langle a_z(\mathbf{r}); t \rangle + \dots
 \end{aligned} \tag{79}$$

The functional derivatives are

$$\begin{aligned}
 & \left(\frac{\delta\rho_{0\ell}}{\delta\langle a_z(\mathbf{r}'); t \rangle} \right)_{\delta\langle a_z; t \rangle=0} = \delta(\mathbf{r}' - \mathbf{r}) \left(\frac{\partial\rho_0(\langle a_z(\mathbf{r}); t \rangle)}{\partial\langle a_z(\mathbf{r}); t \rangle} \right. \\
 & \quad \left. + \frac{\partial\mathbf{m}_\beta(\mathbf{r}, \langle a_z(\mathbf{r}); t \rangle)}{\partial\langle a_z(\mathbf{r}); t \rangle} \cdot \nabla \langle a_z(\mathbf{r}); t \rangle \right) \\
 & \quad + \mathbf{m}_z(\mathbf{r}, \langle a_z(\mathbf{r}); t \rangle) \cdot \nabla \delta(\mathbf{r}' - \mathbf{r}) + \dots
 \end{aligned} \tag{80}$$

Here,

$$\begin{aligned}
 & \mathbf{m}_\beta(\mathbf{r}, \langle a_z(\mathbf{r}); t \rangle) \\
 & \equiv \int d\mathbf{r}' \left(\frac{\delta\rho_{0\ell}}{\delta\langle a_\beta(\mathbf{r}'); t \rangle} \right)_{\delta\langle a_z; t \rangle=0} (\mathbf{r}' - \mathbf{r}),
 \end{aligned} \tag{81}$$

and $\rho_0(\langle a_z(\mathbf{r}); t \rangle)$ is the actual HCS with its global density, energy, and momentum evaluated at the common values $\langle a_\alpha(\mathbf{r}); t \rangle$. It follows from (32) that the averages of $A_\alpha(\mathbf{r})$ for ρ , $\rho_{0\ell}$, and ρ_0 are all the same. This in turn gives

$$\int d\Gamma a_\alpha(\mathbf{r}) \mathbf{m}_\beta = 0 = \int d\Gamma a_\alpha(\mathbf{r}) \Delta. \quad (82)$$

With these results and the fact that Δ is of first order in the gradients, (78) to first order in the gradients becomes

$$\begin{aligned} & \int d\mathbf{r}' \frac{\delta \rho_{0\ell}}{\delta \langle a_\alpha(\mathbf{r}'); t \rangle} \left\{ \nabla \cdot \langle \mathbf{b}_\alpha(\mathbf{r}); t \rangle \right. \\ & \quad \left. + \delta_{\alpha 2} \langle w(\mathbf{r}); t \rangle \right\} - \bar{L} \rho_{0\ell} \\ & \rightarrow \bar{L} \rho_0 - (1 - \mathcal{P}) (1\bar{L} + K^T)_{\alpha\beta} \mathbf{m}_\beta \cdot \nabla \langle a_\alpha; t \rangle \\ & \quad + \mathcal{P} \bar{L} \Delta. \end{aligned} \quad (83)$$

The matrix K^T is the transpose of K .

$$K_{\alpha\beta} = \delta_{\alpha 2} \frac{\partial \omega(\langle a_\alpha(\mathbf{r}); t \rangle)}{\partial \langle a_\beta(\mathbf{r}); t \rangle}, \quad (84)$$

and I is the unit matrix. The generator $\bar{L}$ is the same as that of (12) with $\omega \rightarrow \omega_0(\langle a_\alpha(\mathbf{r}); t \rangle)$ for the HCS evaluated at the common values $\langle a_\alpha(\mathbf{r}); t \rangle$

$$\bar{L} = -\omega_0(\langle a_\alpha(\mathbf{r}); t \rangle) \partial_{\langle a_\alpha(\mathbf{r}); t \rangle} + \bar{L}. \quad (85)$$

Finally, $\mathcal{P}$ is the projection operator

$$\mathcal{P}X = \frac{\partial \rho_0}{\partial \langle a_\alpha(\mathbf{r}); t \rangle} \int d\Gamma a_\alpha(\mathbf{r}) X. \quad (86)$$

The first term of (83) vanishes by definition of the HCS, ρ_0 , confirming that the right side of the Liouville Eq. (34) is of first order in the gradients.

At this point, the Liouville Eq. (34) becomes

$$\begin{aligned} & \partial_t \Delta - \int d\mathbf{r}' \frac{\delta \Delta}{\delta \langle a_\alpha(\mathbf{r}'); t \rangle} \omega_0(\langle a_\alpha(\mathbf{r}'); t \rangle) + \mathcal{P} \bar{L} \Delta \\ & = (1 - \mathcal{P}) \mathbf{Y}'_\alpha \cdot \nabla \langle a_\alpha; t \rangle, \end{aligned} \quad (87)$$

$$\mathbf{Y}'_\alpha \equiv -(I\bar{L} + K^T)_{\alpha\beta} \mathbf{m}_\beta. \quad (88)$$

This equation is still exact up through contributions of first order in the gradients. It has solutions of the form

$$\Delta(\Gamma, t | \langle a_\alpha(\mathbf{r}); t \rangle) = \mathbf{G}_v(\Gamma, t, \langle a_\alpha(\mathbf{r}); t \rangle) \cdot \nabla \langle a_v(\mathbf{r}); t \rangle, \quad (89)$$

Substitution into (87) gives the corresponding equation for $\mathbf{G}_v$

$$\partial_t \mathbf{G}_v + (1 - \mathcal{P}) (1\bar{L} + K^T)_{v\beta} \mathbf{G}_\beta = (1 - \mathcal{P}) \mathbf{Y}'_v, \quad (90)$$

with the solution

$$\begin{aligned} & \mathbf{G}_v(\Gamma, t, \langle a_\alpha(\mathbf{r}); t \rangle) \\ & = \int_0^t dt' \left(e^{-(1-\mathcal{P})(1\bar{L}+K^T)t'} \right)_{v\beta} (1 - \mathcal{P}) \mathbf{Y}'_\beta. \end{aligned} \quad (91)$$

It is possible to add to (87) an arbitrary solution to the homogeneous equation corresponding to (90). As described in the text, this represents the dynamics of the first stage of rapid velocity relaxation to the local HCS. The interest here is in the second stage where possible formation of a normal solution occurs. Hence, it is simpler to choose that stage for initial conditions (initial local HCS).

Define the derivatives of the HCS by

$$\Psi_\beta(\Gamma, \langle a_\alpha(\mathbf{r}); t \rangle) \equiv \frac{\partial \rho_0}{\partial \langle a_\beta(\mathbf{r}); t \rangle}. \quad (92)$$

Then differentiate the equation for ρ_0

$$\frac{\partial}{\partial \langle a_\beta(\mathbf{r}); t \rangle} \bar{L} \rho_0 = 0, \quad (93)$$

to get

$$(I\bar{L}_T + K^T)_{v\beta} \Psi_\beta = 0. \quad (94)$$

Since $(I\bar{L}_T + K^T)$ is the generator for the dynamics in (91) this shows that Ψ_β are the invariants of that dynamics.

The projection operator $\mathcal{P}$ in (95) acts only on phase functions with translational invariance. In that case (86) simplifies to

$$\mathcal{P}X = \Psi_\beta \int d\Gamma A_\beta X, \quad A_\beta = V^{-1} \int d\mathbf{r} a_\beta(r). \quad (95)$$

The first equality of (82) becomes $\mathcal{P} \mathbf{m}_\beta = 0$. This in turn gives

$$\mathbf{m}_\beta = (1 - \mathcal{P}) \mathbf{m}_\beta = (1 - \mathcal{P}) \mathbf{M}_\beta, \\ \mathbf{M}_\beta \equiv \int d\mathbf{r}' \left(\frac{\delta \rho_{0\ell}}{\delta \langle a_\alpha(\mathbf{r}'); t \rangle} \right)_{\delta \langle a_\alpha; t \rangle = 0} \mathbf{r}'. \quad (96)$$

Then $(1 - \mathcal{P}) \mathbf{Y}'_\alpha$ simplifies to

$$(1 - \mathcal{P}) \mathbf{Y}'_\alpha = -(1 - \mathcal{P}) (\mathcal{I}\bar{\mathcal{L}} + \mathbf{K}^T)_{\alpha\beta} (1 - \mathcal{P}) \mathbf{M}_\beta \\ \equiv (1 - \mathcal{P}) \mathbf{Y}_\alpha \quad (97)$$

with

$$\mathbf{Y}_\alpha = -(\mathcal{I}\bar{\mathcal{L}} + \mathbf{K}^T)_{\alpha\beta} \mathbf{M}_\beta. \quad (98)$$

Use has been made of the identity

$$(1 - \mathcal{P}) (\mathcal{I}\bar{\mathcal{L}} + \mathbf{K}^T) \mathcal{P} = 0. \quad (99)$$

This same identity leads to a simplification of the dynamics in (91)

$$e^{-(1-\mathcal{P})(\mathcal{I}\bar{\mathcal{L}}+\mathbf{K}^T)t'} (1 - \mathcal{P}) \\ = (1 - \mathcal{P}) e^{-(\mathcal{I}\bar{\mathcal{L}}+\mathbf{K}^T)t'} (1 - \mathcal{P}). \quad (100)$$

In summary, the solution to the Liouville equation to first order in the gradients is

$$\rho(\Gamma, t | \langle a_\alpha; t \rangle) = \rho_0(\Gamma, \langle a_\alpha(\mathbf{r}); t \rangle) \\ + (1 - \mathcal{P}) (\mathbf{M}_\beta(\Gamma, \langle a_\alpha(\mathbf{r}); t \rangle) \\ + \int_0^t dt' \left(e^{-(\mathcal{I}\bar{\mathcal{L}}+\mathbf{K}^T)t'} \right)_{v\beta} \\ \cdot (1 - \mathcal{P}) \mathbf{Y}_\beta(\Gamma, \langle a_\alpha(r); t \rangle)) \\ \cdot \nabla \langle a_v(r); t \rangle. \quad (101)$$

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Statistical Mechanics of Clogging

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Article Outline

Glossary
Definition of the Subject
Introduction
Clogging
Unclogging
Summary and Discussion
Future Directions
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Glossary

Arch Set of mutually stabilizing particles, meaning that if any one of them is removed the whole set will collapse.

Clogging Halt of the flow of macroscopic particles caused by the development of a local structure (an arch in two dimensions or a dome in three) which brings the whole system to a rest state.

Granular matter Material composed of independent, macroscopic particles that interact solely by contacts or collisions. As the latter are intrinsically dissipative, energy is not conserved, and therefore, the system typically adopts metastable configurations.

Granular Silo Container in which granular matter is stored. The emptying of silos is generally performed through an orifice at the bottom, although other alternatives (such as the discharge through lateral orifices or by means of extraction belts) are also possible.

Unclogging Destabilization of a clogging arch by means of an energy input which must be external for the case of inert granular media, but can be also internal for other systems such as active matter.

Definition of the Subject

Clogging is defined as an arrest of the flow of macroscopic particles caused by the formation of a local arrangement that is generally metastable. Usually, clogging occurs at bottlenecks when the neck-to-particle size ratio is slightly above the unity. Although clogs may appear in a wide variety of systems – such as cells, colloids, or live beings – we will focus here on clogging in granular matter as a prototypical and simple case. Understanding clogging in granular systems is important from the industrial and environmental viewpoint. Indeed, clogging in silos or hoppers may completely halt a production line in food or pharmaceutical industries. Also, a safe and efficient handling of raw materials in mining is important to prevent environmental harm and to reduce production costs. But even in granular matter, understanding clogging poses a tough challenge as the arch formation is essentially a local phenomenon that drives the whole system to a sudden arrest. Contrary to other physical processes like jamming, the definition of average magnitudes – such as volume fraction, for instance – is not straightforward.

Clogging is intimately related to the formation of arches and their stability. Therefore, introducing an excitation at the outlet or nearby can be a suitable strategy to destroy the clog and resume the flow. Thus, when a vibration is applied at the bottom of a silo, the flow may become intermittent resembling the dynamics observed in other active systems flowing through constrictions. The physics underlying clogging, on one side, and unclogging, on the other side, is not the same, as

revealed by the different nature of their statistical properties. In the following sections we will deep into this question and others, such as the arguments on the existence or not of a critical outlet size above which clogging is not possible, a subject discussed since mid last century.

Introduction

The dense flow of granular materials through a narrowing is a complex situation. At the bottleneck, the system undergoes a transition from fluid like behavior (above the opening) to gas like behavior (after the neck, where the contacts among particles are sparse). This flow becomes even more complicated when the aperture is only a few times larger than the typical particle size; in this scenario there exists the possibility that a metastable structure forms spanning the whole outlet, causing a complete arrest of the grains.

Although by the end of the last century an abundant number of devices were created – and even patented – to prevent clogging, the problem fundamentals were only scarcely studied at that time. As a matter of fact, most of the works were aimed at determining the size of the outlet that guaranteed a continuous flow through the silo outlet (Arnold and McLean 1976; Drescher et al. 1995; Jenike 1964; Walker 1966). Conversely, there was a remarkable interest on investigating the flow properties in the silo discharge; the focus was mostly put on the flow rate dependence on the outlet size (Beverloo et al. 1961). In most cases, the orifices were large enough to prevent clogging, which was considered as an aside problem to be avoided. Indeed, from an applied point of view, clogging avoidance was the main concern at that time and this is reflected on the focus of the investigations that were performed.

In the last two decades, the study of clogging in granular silos has regained the attention of the scientific community. Among others, two reasons may be pointed out for this appealing. First, clogging is an apparently simple everyday problem (we all have to shake the saltcellar to pour salt in our food) with a fundamental interest, where deep questions arise, and it is accessible to researchers

with limited resources. Second, given the inert nature of the grains, clogging in silos has been taken as a standard against which to compare clogging in other, more complex systems. As examples, we pinpoint the flow through bottlenecks of colloids, microbial populations, mechanically self-driven robots, suspensions, pedestrians, animals, and other kinds of active matter. Given the different nature of the particles composing these systems, it becomes obvious that the analogies are only qualitative; despite this, some of the models and analytical approaches introduced for the granular case can be used as a starting point for more sophisticated elaborations pertinent to those other systems.

Remarkably, the number of applications in which clogging is a paramount concern is much larger if all these related many-body systems are included. For example, clogging of a dense micro-particle suspension can occlude microchannel constrictions, a behavior that is exploited in medicine to provoke embolization of blood vessels in order to shrink a tumor. Besides, the formation of clogs in suspensions of larger particles is crucial in determining the lifetime of subsurface flow treatments, a widely used alternative to remove pollutants from wastewater. Similarly, clogging of suspended hydrated particles is a major issue concerning oil and gas transport through pipelines. A reasonable understanding of clogging is also necessary to guarantee a good performance of slit-structures, which are rigid barriers with one or more slits built in craggy mountains to reduce avalanche hazard. Last but not least, clogging has also occasionally happened in crowds trying to evacuate enclosed areas in highly competitive and dire situations.

In all the examples given above, a geometrical constriction (i.e., a bottleneck) is at play. However, it has been recently shown that this specific geometry is not imperative to observe clogging. Indeed, if the particles are sufficiently confined, a blockage may also show up in a straight channel. This happens for instance in underground mining, where raw materials driven by gravity are conveyed through vertical pipes from one level of the mine to another. In this case, the blocking arches do not rest on the silo bottom or hopper

walls, but lean against the vertical walls of the pipe. This is possible due to frictional forces, and the effect is magnified because of the geometrical frustration introduced by the flat faceted stones that are typically transported in these channels. Although here we will focus on the bottleneck geometry, several works about clogging in straight channels and obstacle arrays – an interesting configuration that may turn out to be useful for linking clogging and jamming behavior – will also be described.

Clogging

Clogging as a Stochastic Process

Let us consider a container full of grains discharged through an orifice at the bottom which is only a few times larger than the typical particle size. In this scenario, the probability that a clogging arch develops is constant over time, that is, it is a Poisson process. This fact implies that:

1. There is no way to predict exactly when the system will get clogged.
2. Clogging is a history independent process: even if the system has been flowing for a lot of time, the probability of getting clogged remains the same.
3. If we define the avalanche size as the number of grains flowing out the silo before an arch

clogs it, the distribution of these sizes will follow an exponential tail.

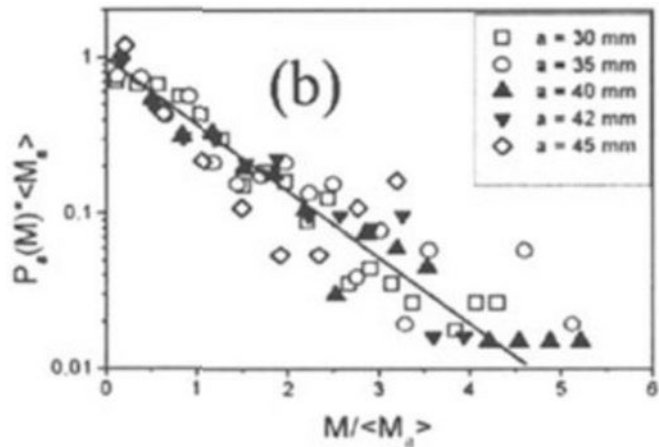
4. There is no correlation among the size of consecutive avalanches.
5. The average avalanche size is well defined.

The first evidence of the exponential nature of the avalanche size distribution was reported by Clément et al. (2000) as shown in Fig. 1. Subsequently, Zuriguel et al. corroborated this feature and provided an interpretation in terms of a probabilistic model (Zuriguel et al. 2003). The idea was to assign the same probability of clogging p_c to all particles inside the silo. Therefore, the probability that a particle passes through the outlet without forming a clog can be written as $p_p = 1 - p_c$, and the probability of getting an avalanche of s particles can be described by Eq. 1 (note that the original equation proposed was $n(s) = p_p^s p_c^2$ as it was considered also the precedent clogging event but it was posteriorly (Zuriguel et al. 2005) corrected to Eq. 1).

$$n(s) = p_p^s p_c \quad (1)$$

That is, the probability of getting an avalanche of size s is obtained by multiplying s times the probability that a particle passes through the exit and one time the probability that the particle clogs it. This definition allows a straightforward connection between the first moment of the

Statistical Mechanics of Clogging, Fig. 1 Rescaled mass distributions of avalanches for different outlet sizes a , as indicated in the legend. $P_a(M)$ is the probability density for an avalanche with mass M for an outlet size a . The average avalanche mass is $\langle M_a \rangle$. The solid line displays an exponential decay. (Reprinted from Clément et al. (2000))



distribution (the mean avalanche size) and p_c (Janda et al. 2008):

$$\langle s \rangle = \frac{p_p}{p_c} \quad (2)$$

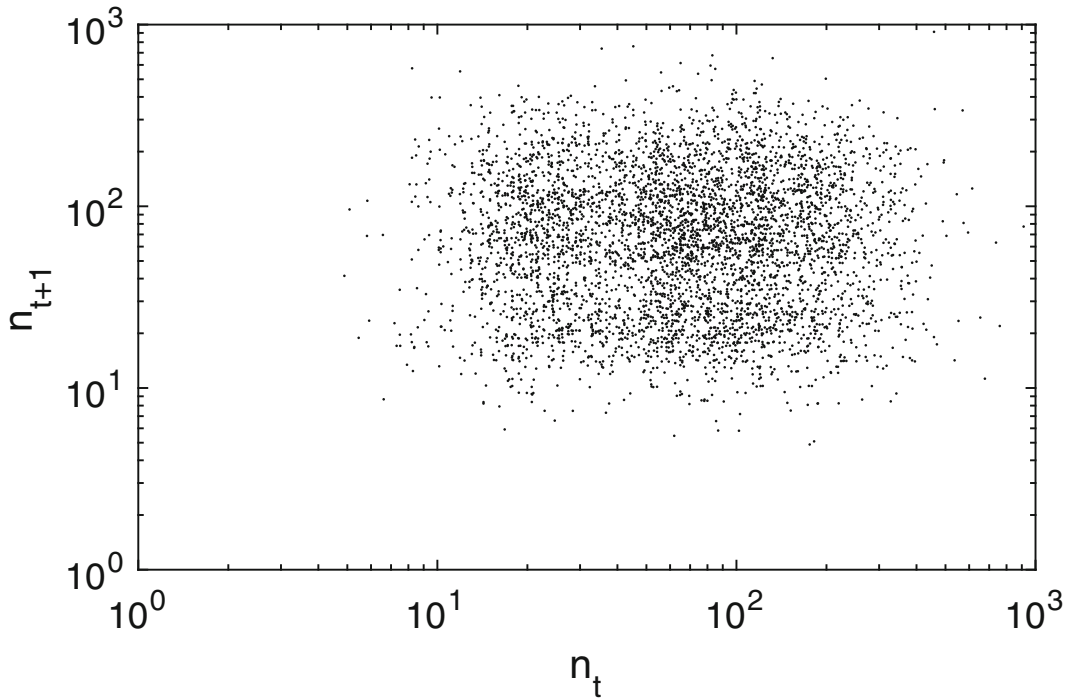
In most of the scenarios investigated the avalanches are larger than about 100 particles. In this case $p_p \simeq 1$, and therefore $\langle s \rangle \simeq p_c^{-1}$.

Another salient feature reported in Zuriguel et al. (2003) was the apparent lack of correlation among the size of consecutive avalanches (see Fig. 2). If we accept the hypothesis of lack of memory in the passage of particles within a single avalanche, it is not surprising that the statistics of consecutive avalanches are independent.

Although the probabilistic model leading to Eq. 1 was obtained by assigning to each particle a given probability of forming a clog, the same reasoning is valid if groups of particles are considered instead, as stated in Zuriguel et al. (2003).

Indeed, it is obvious that the development of a clogging arch is a process involving several particles. In order to account for this issue, Masuda et al. (2014) devised a model in which the arch formation region was split into discrete sites that can contain at most one particle. By defining a particle inflow rate α and different outflow rates depending on the occupancy of neighboring sites (see Fig. 3), different dynamics were observed including flow intermittency and clog formation. The latter occurred when all sites were filled. Remarkably, this model recovers the exponential distribution of avalanche sizes.

A similar approach of dividing the space in cells was in fact implemented a decade before by Helbing and coworkers in a work (Helbing et al. 2006) where they presented an analytical model which served for both granular bottleneck flows and pedestrian escape dynamics through a narrowing. Based on a continuity equation in polar coordinates, they observed shockwaves

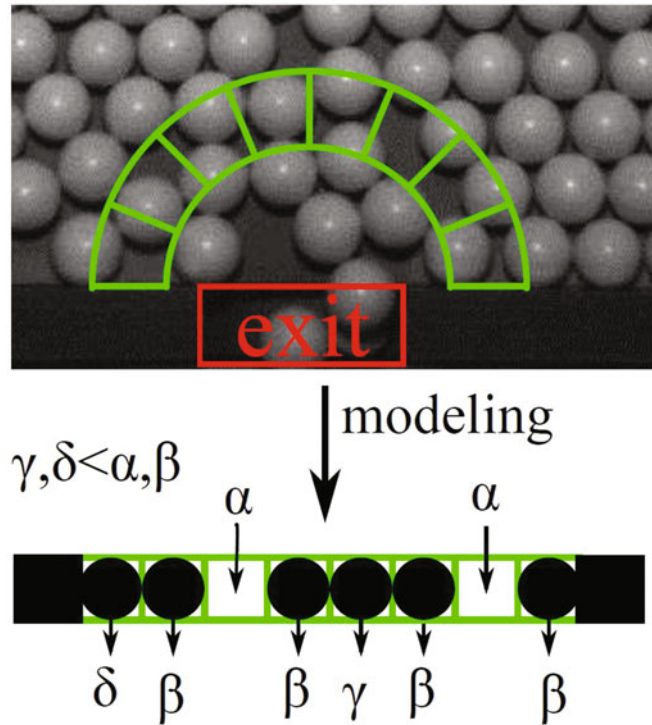


Statistical Mechanics of Clogging, Fig. 2 First return map of avalanche sizes, that is, the avalanche size $n_t + 1$ vs. the previous avalanche size n_t , where t is a correlative

index ordering the sequence of avalanches. (Reprinted from Zuriguel et al. (2003))

Statistical Mechanics of Clogging, Fig. 3

Arch formation model in which the arch region is divided in several cells of about the size of a particle (top). In the bottom, one-dimensional projection of the arch where arrows into a site represent a particle “inflow” at a rate α . The arrows pointing out of sites indicate the “outflow” which is defined by three-site interactions. When a filled site is besides an empty site, the outflow rate is defined by β . When a filled cell is surrounded by two filled cells, the outflow rate is γ ; and when a filled cell is between a filled cell and a boundary, the outflow rate is δ . (Reprinted from Masuda et al. (2014))



when the inflow exceeds the maximum outflow. More importantly for the case we are analyzing here, their model gave rise to three different regimes depending on the exit size: no flow for small exits, intermittent flow for medium size doors, and continuous flow for large enough openings. In the intermittent flow scenario, exponentially distributed avalanche sizes were reported in good agreement with experimental data.

Up to now, we have described several works where the exponential distribution of avalanche sizes is observed and explained in different, but similar, ways. All share the idea that clogging is a stochastic process where the probability of a clog depends on the outlet size, as will be explained below. The exponential distribution of avalanches is considered as a hallmark of the flow of discrete particles through bottlenecks and has been also reproduced by many authors in different geometries and scenarios (Kondic 2014; Pérez 2008; Sheldon and Durian 2010). Nevertheless, there is an exception to this accepted rule: when the orifice is strongly asymmetric the avalanche statistics resemble more a power law than an exponential

distribution. This was discovered by Saraf and Franklin when working with wedge hoppers having an orifice that was around 20 times longer than wider (Saraf and Franklin 2011). The explanation given for this feature assumed that the clogging probability of strings of particles depends on their orientation. By considering a uniform distribution of probabilities and integrating over all the allowable string orientations, an expression is obtained for the avalanche size distribution that depends on the exit geometry. In particular, the well-known exponential distribution is generated for isometric (round) orifices, whereas for anisometric exits the expression tends to an asymptotic value that scales as $n(s) \sim s^{-2}$.

Does a Critical Outlet Size Exist?

The supply of a continuous flow of grains through the orifice (i.e., preventing clog formation) was the ambition of the pioneering engineers who studied silo clogging. For this reason, the research since the 1960s has been primarily focused in finding the outlet size that guaranteed a complete

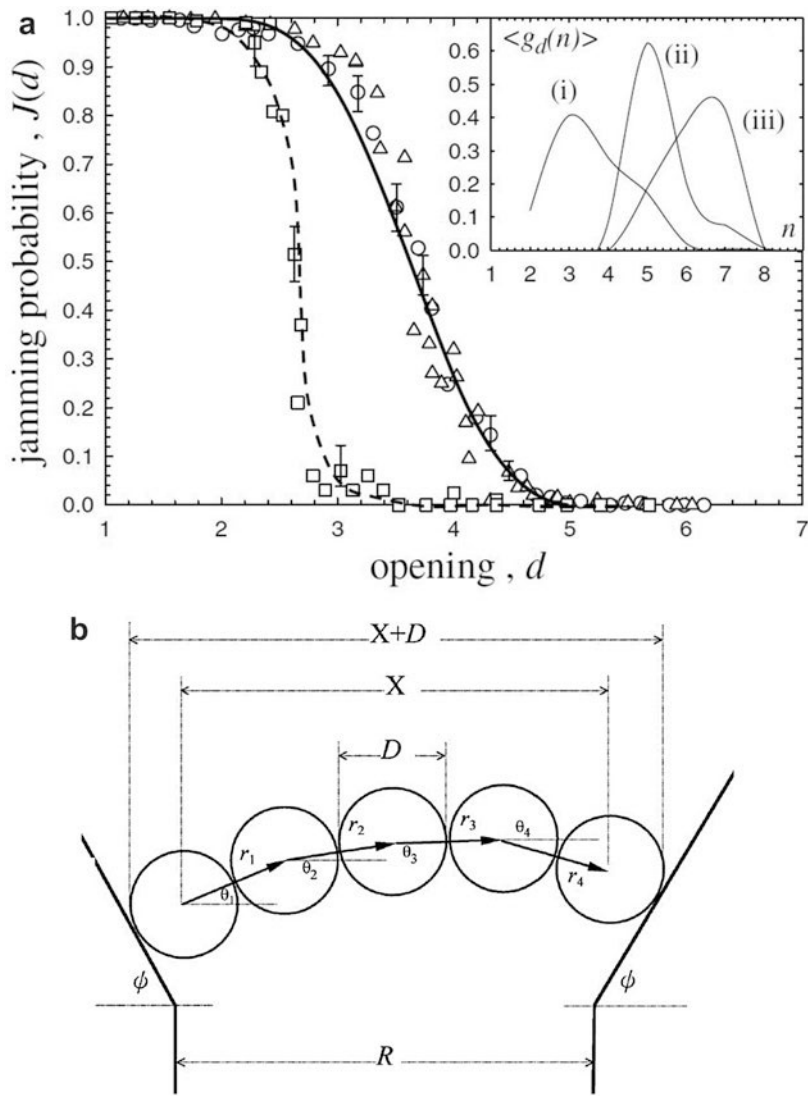
absence of clogging (Arnold and McLean 1976; Drescher et al. 1995; Jenike 1964; Walker 1966). The approach followed in these works was to set up the stress-strain rate relations and analyze the critical factors which ensured continuous gravity flow. From this, a typical orifice value of around 5 to 10 times the particle size was found for non-cohesive grains.

Instead, modern approaches involve statistical analysis of the avalanche sizes or clogging probability, and their dependence on the outlet size. In the following subsection we summarize some recent advances in this area.

Statistics of Avalanches

In their trailblazing work K. To et al. (2001) measured a quantity they called J – the probability that a two-dimensional silo filled with a fixed number of grains gets jammed before emptied – for different outlet sizes (Fig. 4). The most salient feature they observed was a strong dependence of J on the outlet size, which suggested a transition to a state where $J = 0$ (i.e., complete absence of clogging) for an opening size of around 5 to 7 particle diameters. In order to describe this transition, the authors developed a model in which the clogging arch was envisaged as a restricted random

Statistical Mechanics of Clogging, Fig. 4 Left: probability that a silo gets jammed J versus the outlet size. Data correspond to hoppers of different angles ϕ : circles ($\phi = 34^\circ$), triangles ($\phi = 60^\circ$), and squares ($\phi = 75^\circ$). Right: Sketch of an arch clogging a hopper of angle ϕ with an exit size R . The angles among consecutive particles are defined, from left to right, as $\theta_1, \theta_2, \dots, \theta_{n-1}$. (Reprinted from To et al. (2001))



walker. In this model, the particles conforming the arch took random positions with some restrictions:

1. The random walker goes from left to right.
2. The arch has to be convex at all sites to guarantee its stability.
3. The particles cannot interpenetrate each other.
4. The total span of the arch has to be larger than the outlet size.

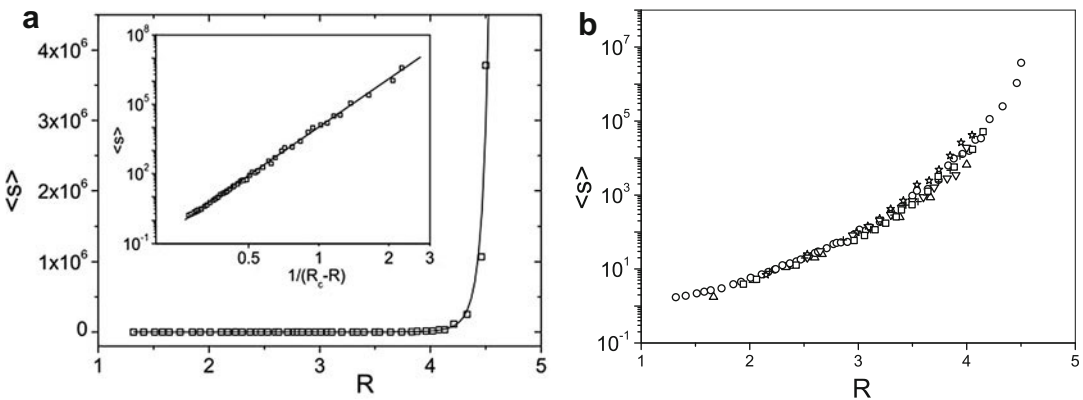
This model successfully described the jamming probability dependence on the outlet size for the experimental conditions implemented in that work, showing values of J tending to zero for large enough outlet sizes. However, the question about the existence of a transition (in the thermodynamic sense) from a jammed state to an unjammed one remained open.

This problem was approached by Zuriguel et al. (2005), who used a three-dimensional silo to experimentally investigate the clogging probability in a wide range of outlet sizes, including some cases with a very low probability of clogging. Remarkably, they explored outlet sizes in which the mean avalanche size was above 10^6 particles and proposed Eq. 3 as the best fitting expression for their data. As it is evidenced in Fig. 5, the fitting was quite good with the following parameter values: $\gamma = 6.9 \pm 0.2$, $A = 9900 \pm 100$,

and $R_c = 4.94 \pm 0.03$. Notably, the figure obtained for the critical outlet size was similar to previous predictions based on the stress-strain rate relations reported at the end of the twentieth century. The unusually high value of the exponent, apart from manifesting the strong dependence of the avalanche size on the outlet size, also hinted to the need of looking for another order parameter (instead of the avalanche size) that better describes the clogging transition. In addition, it was shown that R – the outlet size rescaled by the particle diameter – is the most important parameter on determining the clogging probability. In fact, experiments with different outlet sizes and particle diameters, but the same R , displayed very similar results (Fig. 5, right). Also, the effect on clogging of the material properties of the particles was revealed to be rather small.

$$\langle s \rangle = \frac{A}{(R_c - R)^\gamma} \quad (3)$$

Shortly after the introduction of this power law fit, K. To suggested that two other expressions were able to fit the data equally well (at least for experiments in two-dimensional silos) (To 2005). One of such expressions (Eq. 4) was a stretched exponential which did not involve a critical outlet size. Later on, this result was given additional



Statistical Mechanics of Clogging, Fig. 5 Left: mean avalanche size versus the exit size R . In the inset, mean avalanche size versus $(R_c - R)^{-1}$ in logarithmic scale. In both cases the fit corresponds to Eq. 3 with the parameters indicated in the text. Right: mean avalanche size vs R in

semilogarithmic scale; data correspond to spherical grains of different materials (delrin, glass, lead, and steel) and different particle diameters (from 1 to 3 mm). (Reprinted from Zuriguel et al. (2005))

support by Janda et al. (2008) for the two-dimensional case, a scenario for which the origin of the equation was related with the statistics of the arch lengths obtained in static deposits of grains. Nevertheless, the goodness of Eq. 4 to fit the outcomes of a three-dimensional silo was challenged, suggesting that the fitting was neither satisfactory when raising R to a power of 3 (the dimension of the system).

$$\langle s \rangle = A e^{BR^2} \quad (4)$$

Following another line of reasoning, Thomas and Durian (2015) build upon experimental data of avalanche sizes in a wide variety of situations (hoppers with several tilt angles, orifices with different geometries, particles of diverse nature, and so on) to show that the three fitting expressions proposed by K. To worked nicely in three

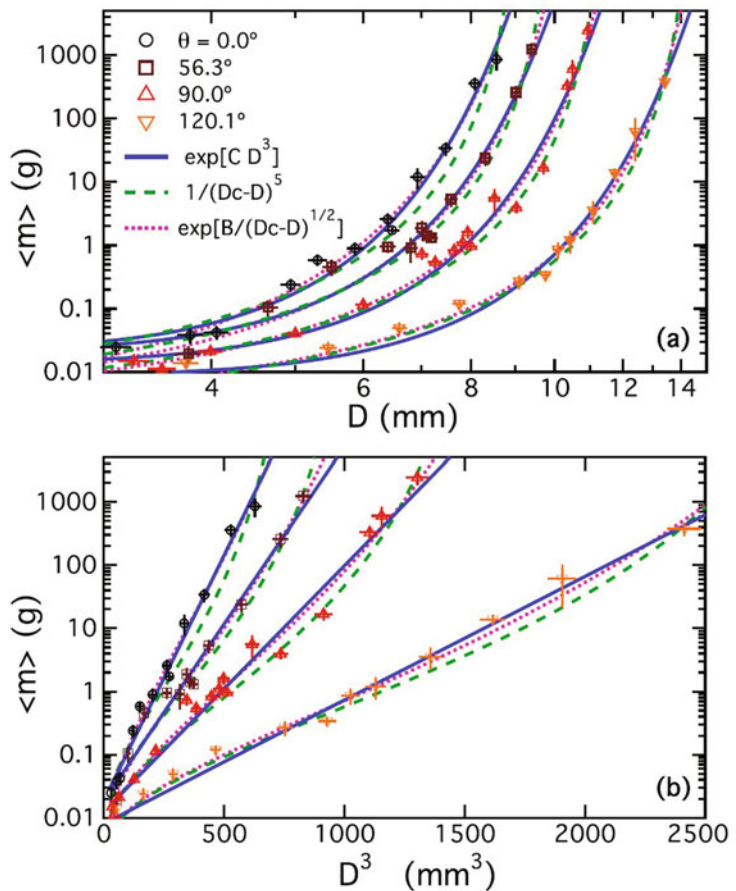
dimensions (Fig. 6). Moreover, the origin of the $\langle s \rangle = Ae^{BR^3}$ relationship was justified by considering all possible arch configurations and evaluating the amount of them that would be effectively able to block the orifice. The same approach was afterwards further elaborated by researchers of the same group (Koivisto and Durian 2017) to successfully evaluate the effect of interstitial fluid on the clogging probability.

Dynamical Signatures of Clogging

An alternative way of approaching the question of whether there is a critical outlet size above which clogging would never happen is to look for dynamical flow features that could reveal any difference at both sides of the hypothetical transition point. The first proof of the existence of such differences was reported by Longhi et al. (2002) in a work where they characterize the impulses delivered to the wall

Statistical Mechanics of Clogging, Fig. 6

Left: mean avalanche size (in grams) versus the exit size. Data for hoppers with different tilt angles as indicated in the legend. The three line types represent different fitting alternatives. Right: the same data and fits using the outlet size raised to the third power in the abscissa axis. (Reprinted from Thomas and Durian (2015))



of a 2D hopper. They found that the distribution of impulses decayed exponentially for impulses above the average, in the same way that the forces in a static granular packing do (Mueth et al. 1998). This happens independently on the hopper size, which only affects the impulse distribution for values below the average. However, these small impulses display a smooth evolution when going from continuous to intermittently jamming flows; so there was not any signature of a proper clogging transition. Nevertheless, as reported in the same work, the distributions of time intervals among consecutive collisions did hint an approach to jamming as they tend to a power law distribution with an exponent $-3/2$ when the outlet size was progressively reduced (see Fig. 7).

An additional signature of clogging has been identified by analyzing the fluctuations of the flow rate. In this regard, Janda et al. (2009a) implemented high-speed video recordings to detect the passage of every individual grain through the outlet. With this information the flow rate was calculated in very short temporal windows (of the order of 0.1 s) for different outlet sizes. Interestingly, the distributions of the instantaneous flow rate q were Gaussian for large outlet sizes (where clogging never happens), whereas they became strongly asymmetric for small outlet sizes (where clogging eventually occurs). In the latter case, a strong increase of the number of events toward small values of q was found, displaying a peak at $q = 0$ that was related with the formation of unstable clogs (see Fig. 8).

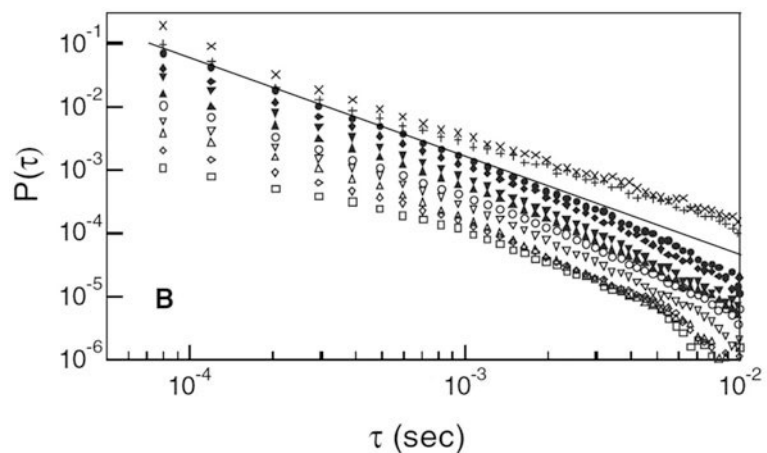
Therefore, a relationship between the appearance of unstable clogs and stable ones was established, and it was suggested that the total absence of unstable clogs for large outlet sizes was reflecting the existence of a “clogging free” region.

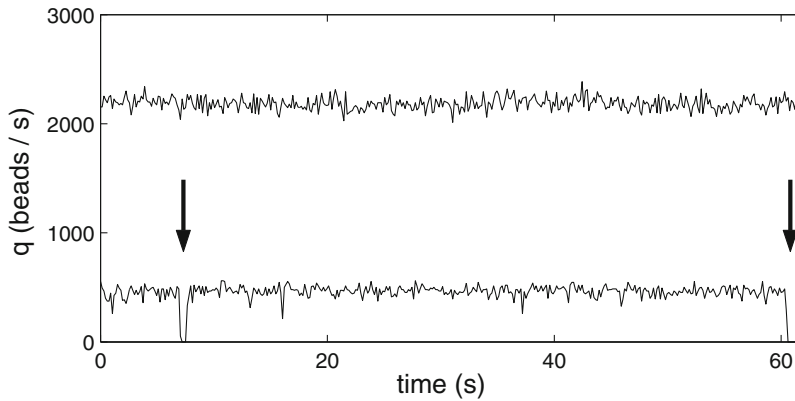
A similar increasing of the fluctuations when reducing the outlet size was reported by Thomas and Durian (2016). In particular, they measured the relative velocity fluctuations and the skewness of the velocity distribution. They also quantified the intermittency by means of a descriptor based on the two-sample Kolmogorov-Smirnov statistic. All these estimators were shown to grow for flows more prone to clogging, that is, when the outlet size was reduced. However, the evolution of these magnitudes with R was smooth and no discontinuity or kink was observed for a hypothetical critical outlet size. Therefore, this analysis undermined the hypothesis of a critical outlet size, supporting instead the notion that clogging is always possible, irrespective of the outlet size.

Incipient Clogging Let us finally mention here a couple of works where different dynamical signatures of incipient clog formation were reported. In 1993, Sakaguchi et al. (1993) suggested that the flow in a 2D silo with a small orifice consisted on an alternation of flows coming from both sides of the outlet. At the instant when the transition (flow from one side to flow from the other side) occurred, the grains collided, thus facilitating the formation of the arches that would lead to clogging. Alternatively, Tewari et al. (2013) performed numerical

Statistical Mechanics of Clogging,

Fig. 7 Logarithmic plot of the probability distributions $P(\tau)$ of the time intervals τ between collisions, for opening sizes ranging from $R = 3$ (top series) to $R = 16$ (bottom). (Reprinted from Longhi et al. (2002))





Statistical Mechanics of Clogging, Fig. 8 Instantaneous flow rate (in number of particles per unit time) measured at short time windows (of 150 ms). The line at the top corresponds to an orifice size of $R = 9.5$, and the one at the

bottom to an orifice of $R = 4.3$. The arrows mark two events where the flow has ceased for a time longer than the window. (Reprinted from Janda et al. (2009a))

simulations of silo discharge and gridded the space into a number of boxes in which the vertical velocity was calculated. Then, the boxes with an instantaneous velocity below half the average were assigned to clusters. From these data, it was observed that just before the appearance of a clog, there was a notable increase of the area covered by these clusters comprising regions with a markedly low velocity. In the same way, after the flow was resumed, the area of these clusters decreased, as displayed in Fig. 9. Moreover, clog formation was associated to the development of vortices at the corners of the hopper that extended inwards, eventually arresting the flow.

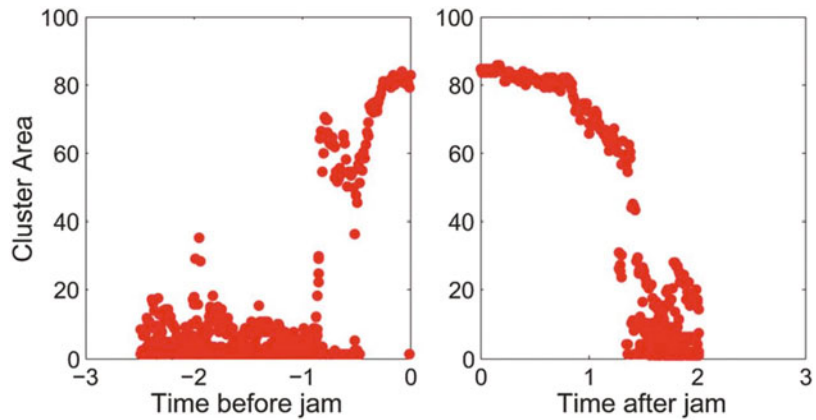
Effect of Other Variables

Clearly, the parameter that mainly determines the clogging probability (and hence, the avalanche size) is the ratio R among the outlet and the particle size. As displayed above (Fig. 5b), its effect is so important that an increase from $R = 3$ to $R = 4$ leads to a growth of the avalanche size by more than 100 times. Due to this dramatic dependence, the main way to analyze the influence of other variables has been to keep a strictly constant outlet size (sometimes a variation of a tenth of millimeter may conceal the effect of other quantities). A time-consuming alternative consists

of repeating a series of experiments for all the range of outlet sizes changing an additional parameter.

The latter was, indeed, the strategy followed by K. To and collaborators to analyze the role of the hopper angle (To et al. 2001). Oddly enough, they observed that for small and medium hopper angles (close to a flat bottomed silo) this parameter had a negligible effect on the probability of clogging ($\phi = 34^\circ$ and $\phi = 60^\circ$ displayed almost the same values). Nevertheless, clogging was dramatically reduced when using a hopper of $\phi = 75^\circ$. This strongly nonlinear dependence has been recently confirmed and explained by considering the angles among the particles conforming the arch (López-Rodríguez et al. 2019) in a two-dimensional silo. This approach revealed that increasing the hopper angle extended the number of forbidden arch configurations, that is, those that would imply interparticle angles that could not be stabilized with typical friction forces. Although this interpretation has not been yet extrapolated to three-dimensional silos, recent results reported in Parretta and Grillo (2019) are perfectly compatible with it. In *Arches* (devoted to the geometry of clogging arches) we will come back to the role of particle angles in the arch stability.

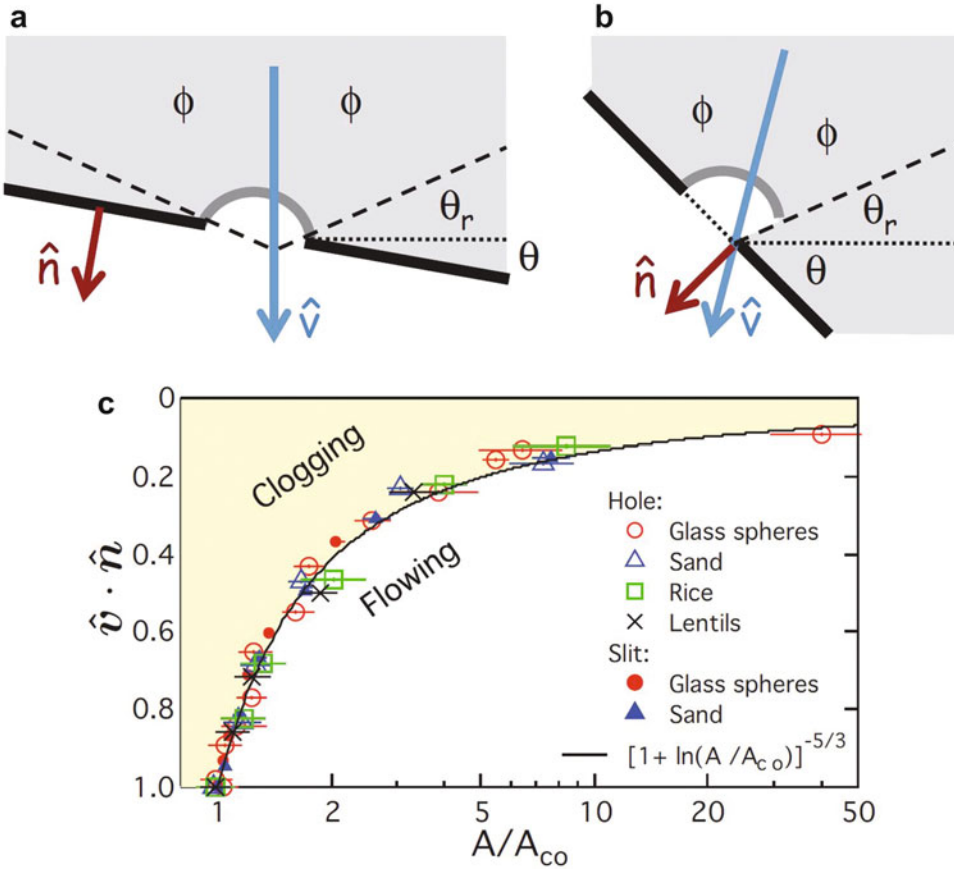
Statistical Mechanics of Clogging, Fig. 9 Temporal evolution of the area covered by connected clusters of low velocity regions (where the vertical velocity is less than half the average) near the orifice. As it can be seen, the area starts growing before the formation of a clog and decreases when the flow is resumed. (Reprinted from Tewari et al. (2013))



A similar line of reasoning could be valid to deal with clogging in lateral and inclined orifices. In two manuscripts from Durian's group (Sheldon and Durian 2010; Thomas and Durian 2013), a clogging phase diagram was suggested when considering its dependence on two parameters: the outlet size and the tilt angle of the silo (Fig. 10). Remark that it is tempting to consider silo tilt as a situation similar to using different hopper angles, but there are conspicuous differences. For instance, it was reported that for a given outlet size the clogging probability grows when increasing the tilt angle (opposite to the hopper case). Moreover, by implementing experiments in both, symmetric orifices (circular) and asymmetric ones (slits), these authors showed that the behavior in all these systems could be encompassed by using the projected area of the aperture over the average flow direction (instead of the gravity direction) as depicted in Fig. 10. In principle, this collapse of the transition points should be also valid for completely vertical orifices, a scenario where the wall width is capital (Davies and Desai 2008; Serrano et al. 2014; Zhou et al. 2017).

Certainly, one of the most surprising features concerning clogging appears when an obstacle is placed above the orifice (Lozano et al. 2012a; Zuriguel et al. 2011). This geometrical constraint, which a priori would restrict the flow of grains, turns to be beneficial if the obstacle position is carefully selected. Indeed, the effect can be utterly remarkable, as in some cases the avalanche size is

increased by more than one hundred times. The physical origin of this behavior was speculated to be related with the arch stabilization process. According to this argument, in a usual silo without an obstacle, a stable arch can develop when a group of particles collides above the orifice due to the confinement imposed by the particles coming from above. On the contrary, for some obstacle positions, there is an effective reduction of pressure above the orifice that allows the colliding particles to be ejected upwards, thus preventing the formation of a stable arch. A demonstration of this behavior was numerically given in Zuriguel et al. (2011) by simulating clogging in silos filled with thin layers of grains. In fact, reducing the height of the granular column inside the silo caused an increase of the mean avalanche size comparable to the one obtained when placing the obstacle. In addition, in Lozano et al. (2012a) it was shown that the clogging reduction effect increased when enlarging the outlet size (see Fig. 11). This can be understood if we consider that the system becomes more sensitive to perturbations when approaching the hypothetical critical outlet size. Although these features were originally reported using a circular obstacle, other authors have implemented different shapes, such as triangular, inverted-triangular, and a horizontal bar (Endo et al. 2017). Among these forms, the triangular obstacle and the horizontal bar were shown to be the most effective to prevent clogging. These authors also attribute the



Statistical Mechanics of Clogging, Fig. 10 Top: sketch of the orifice indicating the unit vectors $\hat{n}$ (normal to the plane of the aperture) and $\hat{v}$ (average flow direction, as defined by bisecting the region where the grains flow) when the tilt angle θ is (a) less than, and (b) greater than, the angle of repose θ_r . Bottom: Clogging transition

diagram for holes and slits and different types of particles. The y-axis is the component $\hat{v} \cdot \hat{n}$ of the unit vectors defined above and the x-axis is the area of the hole normalized by the critical hole area at zero tilt angle. (Reprinted from Thomas and Durian (2013))

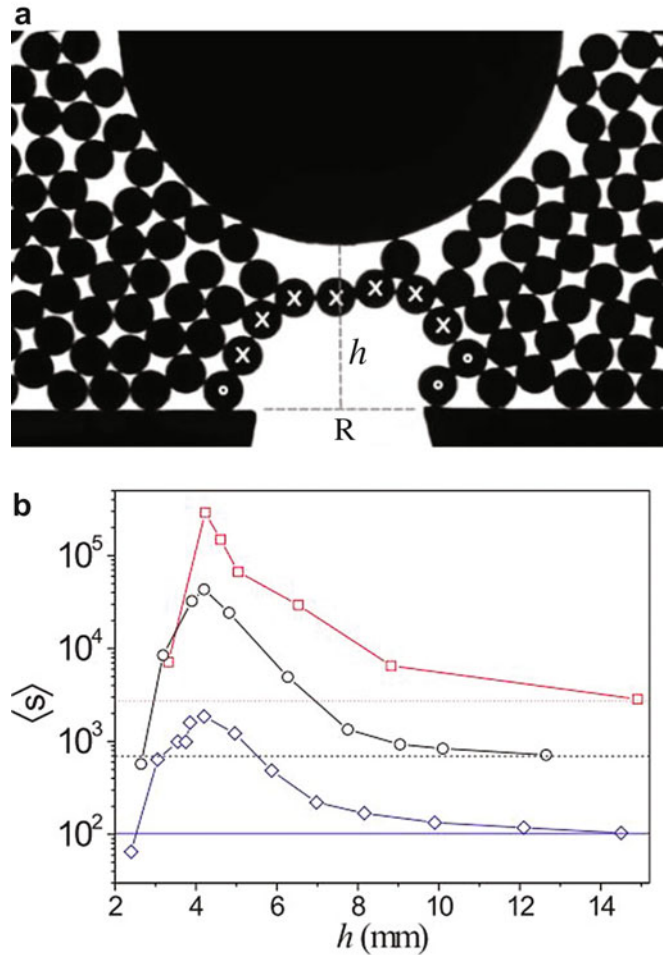
clogging reduction to a decrease in the packing fraction at the exit region. Even though this justification seems different from the pressure reduction explained above, it should be noted that both variables are strongly coupled in granular materials.

Implementing multiple orifices in a silo appears as a natural extension of previous investigations with a single orifice (Kunte et al. 2014; Mondal and Sharma 2014). In this system, if two orifices are sufficiently close to each other, it is possible to obtain an intermittent flow. The reason is that if an arch blocks only one of the orifices, the

flow through the other one can cause the destabilization of the former and restart the flow through it. This behavior has been observed in three- (Mondal and Sharma 2014) and two-dimensional silos (Kunte et al. 2014) and can be used to reduce the overall clogging probability. As could be expected, the distance between both orifices emerges as a key variable. If the orifices are far enough, the effect is negligible and the system behaves as if there were two independent silos; otherwise, when the orifices are close to each other, the interaction becomes increasingly important. Besides, it is interesting to note that the

Statistical Mechanics of Clogging, Fig. 11

Left: photograph of an arch formed above the outlet. R is the length (or size) of the outlet and h is the distance from the bottom of the obstacle to the outlet. Right: mean avalanche size versus the obstacle position for silos with three different outlet sizes (from bottom to top: $R = 3.13$, $R = 4.20$ and $R = 4.55$). The horizontal lines correspond to the mean avalanche size without obstacle for each outlet size. (Reprinted from Lozano et al. (2012a))



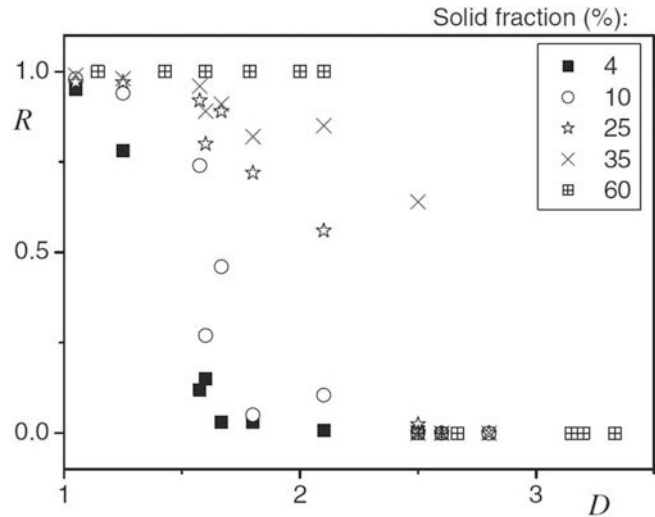
intermittent blocking and unblocking of both orifices can provoke the mixing of the granular matter, as reported in (Kamath et al. 2014).

Another variable that is known to strongly affect the clogging probability and is intimately related with the effect of the obstacle described above is the density of particles in the outlet neighborhood. In fact, if the number of particles above the orifice is controlled by modifying the inflow rate of grains into the silo, it can be observed that there is a threshold value above which the grains start to accumulate. Only in this scenario, and if the orifice is small enough, clogging may appear (Hou et al. 2003; Kohring et al. 1995). In this sense, a connection can be made with an experimental work of

Roussel et al. where a suspension of grains was made to pass through a mesh with a typical hole size slightly larger than the particle size (Roussel et al. 2007). In particular, it was shown that the proportion of material that was trapped in the mesh (called residual R) strongly depended on the hole size but also on the number of particles per volume unit (solid fraction). Indeed, for outlet sizes as small as two times the particle size (where clogging in a standard silo happens very quickly) it was found that R is negligible for 4% solid fraction samples (Fig. 12). This behavior was reproduced with a model in which the likelihood of clogging was linked to the probability that a given number of particles coincide above an orifice; therefore,

Statistical Mechanics of Clogging, Fig. 12

Proportion of material trapped in the mesh (R) as a function of the mesh hole, in a suspension of particles of different solid fractions as indicated in the legend. (Reprinted from Roussel et al. (2007))



higher packing fractions lead to higher probabilities of clogging. The dependence on the outlet size was reproduced by determining that the number of particles necessary to form a clog, n , depended on the hole size as $n = \gamma R^2$. Interestingly, the trend displayed by the residual as a function of R shown in Fig. 12 closely resembles the one reported by To for the probability that a silo with a single orifice jams before emptied (J), as shown in Fig. 4, left. Finally, let us mention that the dependence of the clogging probability on the concentration of particles above the orifice has been also observed in a recent work of Koivisto and Durian, as well as in complementary experiments of fluid driven flow of suspensions through single orifices performed by Wu and coworkers (Guariguata et al. 2012; Lafond et al. 2013).

Regarding the dependence of the clogging probability on the packing fraction above the orifice, Uñac et al. went a step further and revealed the importance of the grain arrangements in the development of clogging inside the silo prior the discharge (Uñac et al. 2012). Their protocol consisted in applying a series of taps of an intensity Γ to a column of grains previous to their discharge through an orifice at the bottom of the column. Remarkably, very low values of Γ – which are known to induce very high values of volume fraction – lead to very small avalanche sizes, that is, high probability of clogging (Fig. 13). Nevertheless, the authors also reported

that samples with the same volume fraction but generated with a different intensity of tapping gave rise to a different clogging probability. This fact revealed that, in very dense granular matter, the volume fraction is not a good macroscopic parameter for predicting the size of the avalanches that would flow through a given aperture.

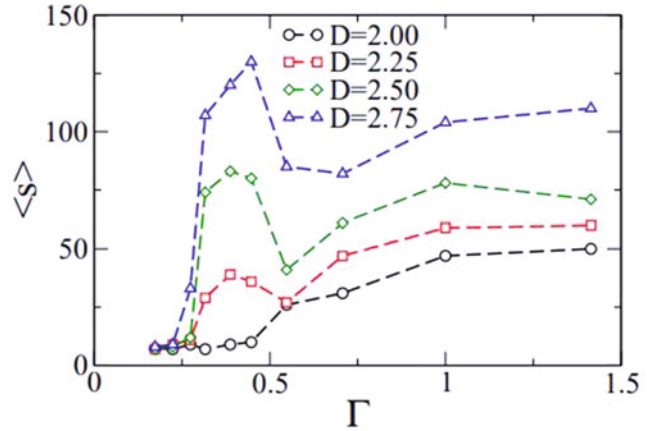
Influence of Particles Properties

Apart from the morphology of the exit or the concentration of particles above the orifice, clogging is also affected by the properties of the grains. After a revision of the articles dealing with this issue, it can be concluded that the shape of the grains and the grain to grain friction are the two most influential ones concerning the development of clogging.

It was K. To in his pioneer work (To et al. 2001) who first analyzed the role of friction in the development of clogging from a statistical point of view. He observed that the probability of clogging increased when using toothed disks instead smooth ones (Fig. 14). This phenomenon was linked to the appearance of local convexities in the arches; that is, particles hanging below the line joining the center of their two neighbors. Of course, these configurations are only possible because of friction. Independent confirmation came a few years later when Pournin et al. studied the effect of friction in a systematic way combining experimental and numerical approaches (Pournin et al. 2007).

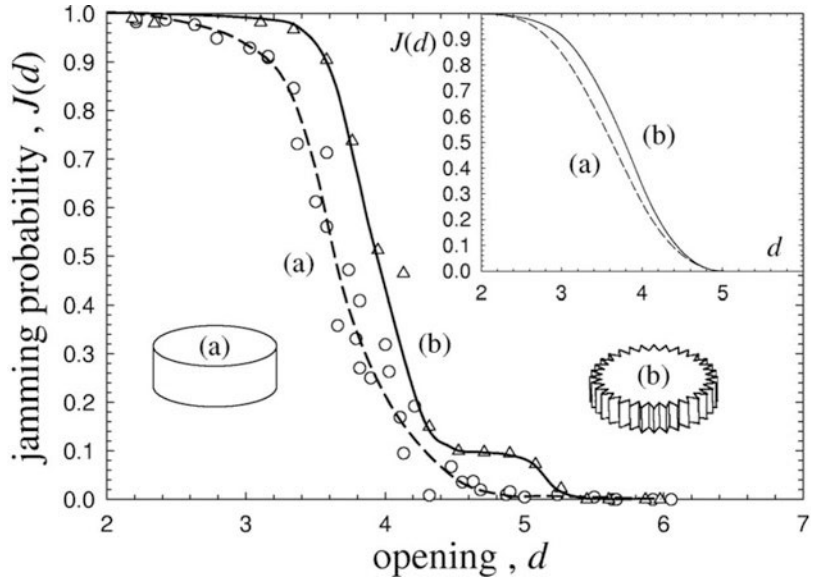
Statistical Mechanics of Clogging, Fig. 13

Mean avalanche size versus the intensity of taps used to prepare the sample before opening the orifice at the bottom. (Reprinted from Uñac et al. (2012))



Statistical Mechanics of Clogging, Fig. 14

Probability that a silo gets clogged before all the grains are discharged for smooth disks (a) and toothed disks (b). (Reprinted from To et al. (2001))



They observed that clogging decreased when reducing the friction coefficient μ ; indeed, for the limit case of $\mu = 0$ (analyzed numerically) clogging was dramatically reduced. Clearly, in this unrealistic situation, arches can only adopt regular shapes, and local convexities are forbidden as it was previously illustrated when inspecting the arches developed in a granular column (Pugnaloni et al. 2006).

Experimentally, this issue was confirmed by using frictionless (or almost frictionless) hydrogel particles (Ashour et al. 2017a; Hong et al. 2017). In these works it was reported that even for very narrow bottlenecks (of around 2 or 2.5 times the

particle size) the probability of clogging was very small. Interestingly, Hong et al. (2017) demonstrated that using droplets (which are frictionless and deformable at the same time) flow can be attained even for an outlet size equal to the particles. In addition, it was shown (Ashour et al. 2017a) that reducing the friction coefficient prevented the pressure saturation at the bottom of the silo, a phenomenon known as the Janssen effect (Janssen 1895).

As mentioned above, the other outstanding property of grains regarding clogging is the particle shape (Ashour et al. 2017b; Goldberg et al.

2018; Tang and Behringer 2016; Vamsi Krishna Reddy et al. 2018). Tang and Behringer observed that clogging in a 2D silo was enhanced when using elliptical cylinders because they align with each other, thus increasing the probability of forming stable arches. Also, they suggested that the relevant particle length scale to compare the behavior of ellipses and isotropic grains is the major diameter of the former, and they demonstrated that the number of particles conforming the arch was considerably higher when using anisotropic grains. In a subsequent work, Ashour et al. (Ashour et al. 2017b) confirmed this observation in a 3D silo, and correlated it with the preference of the elongated particles to orient with the longer axis perpendicular to the clogging dome. This orientation was quantified by using X-ray tomography. Again, in this work it was found that an increasing aspect ratio of the grains leads to higher clogging probabilities compared to spherical grains. Notably, for aspect ratios smaller than 6, the mean avalanche size dependence on the outlet size nicely agreed with the divergent fitting expression (Eq. 3) proposed for discs, which was already found to be valid for rice grains (Zuriguél et al. 2005). Nevertheless, a new feature was discovered for particles with aspect ratios larger than 6: whereas for small outlet sizes the mean avalanche size dependence on the outlet size resembles all the other cases, above a given outlet size the experimental data fall below the expected values given by the fitting curves. For even higher aspect ratios (above 8) the development of rat-holes (completely emptied regions in the central part of the silo surrounded by material close to the lateral wall) strongly alter the clogging dynamics.

Apart from the aspect ratio, another feature of the particle shape that strongly affects clogging is the presence of flat faces (Ahmadi and Hosseini 2018; Goldberg et al. 2018). By means of discrete element modeling, Goldberg et al. evidenced that polygonal particles clogged more easily than discs. Indeed, the polygons that were more prone to clog a two dimensional silo were shown to be the squares, and then hexagons, pentagons, triangles, and heptagons – which displayed a much smaller probability of clogging (close to that of discs). The reason for this

behavior was found to be in the number of side to side contacts among the particles due to shearing forces: squares were the most likely to be aligned and develop this kind of highly stable contact, whereas these configurations were most rare in heptagons. Also, in a recent work in which both gravel and spherical beads were used, more clogging and taller arches were found with gravel (Ahmadi and Hosseini 2018). Interestingly enough, all the results obtained with these different materials have been accounted for using the peak friction angle, which was found to be the main parameter controlling the stability and dimension of the clogging arches.

Finally, let us mention that other variables such as the particle size dispersion (Chevoir et al. 2007; Pournin et al. 2007; Zhao et al. 2019) or the particle size (Gella et al. 2018) have been also shown to affect the clogging probability. Regarding polydispersity, Pournin et al. (2007) performed experiments in a 3D silo with both monodisperse and bidisperse samples, evidencing that jamming mainly depends on the volume averaged diameter of the sample. However, care must be taken when the size difference among the particles is large enough to induce segregation; in this case clogging propensity was enhanced. Opposite to these results, in a recent work based on DEM simulations, Zhao et al. (2019) revealed that increasing the polydispersity of the particle sizes in the silo enhances the probability of clogging. To reach this conclusion, they worked with different samples where the particles distributions were lognormal with the same mean particle size but different standard deviation. Then, although the polydispersity role was shown to be less important than the mean particle size, it was discovered to be relevant for some configurations. Interestingly, the same conclusions were attained a decade before when studying clogging of grains through a sieve (Chevoir et al. 2007).

Role of Dynamics on Clogging

Up to now, all the variables that have been related to clogging concern geometrical features, characterizing either the orifice (where the outlet size is the most influential) or the particles (shape, polydispersity, and so on). Also, the effect of other

parameters such as the volume fraction above the orifice has been identified as potentially relevant. Nevertheless, the role of kinematics in the development of clogging has not been addressed yet, even though the influence of some geometrical aspects of the silo on clogging has been explained through a connection with this parameter. This is the case of a recent work where the influence of the silo width on the clogging probability was linked to an alteration of the particles movement above the outlet (Gella et al. 2017).

Concerning the role of particle dynamics on clogging, Dorbolo et al. performed pioneer silo discharge experiments in high and low gravity conditions, studying gravity values above and below the Earth's gravity (Dorbolo et al. 2013). Although this work was mainly focused on the flow regime (i.e., when clogging does not happen), it was tentatively reported that gravity did not strongly affect clogging behavior. This result was confirmed afterwards by Arévalo et al. (2014), who performed systematic numerical simulations of clogging in a silo with a fixed outlet size (3.5 times the particle size) varying the gravity values over four orders of magnitude. Despite this huge variation, the avalanche size only changed slightly, increasing 1.6 times when going from 0.001 g to 10 g. In a subsequent work, this result was qualified and it was shown that the effect became more important when increasing the outlet size, as it happened with the obstacle effect. For the largest outlet investigated, the avalanche size increased 10 times for the same variation of 4 orders of magnitude in the gravity value. This discovery was explained by portraying the clog formation as a double step process: first, an arch spanning the outlet size must be formed; and second, the arch must resist until the complete dissipation of the kinetic energy in the system. Indeed, this approach allowed estimating the probability that an arch is destabilized, which was shown to primarily depend on the square root of the system kinetic energy.

Following this idea and aiming to design an experiment that better isolates the contribution of the kinematic effects on the clogging process, Gella et al. built a setup consisting of an extracting

belt below the silo orifice. This device allows to control the grain mean velocity without changing the outlet size, effectively decoupling these two variables. Using this strategy, it was revealed that clogging dramatically increases when the grains are discharged at very low velocities (in a quasi-static manner). Moreover, the geometrical and kinetic contributions to the clogging process in a 2D silo were nicely decoupled and described by an expression (Eq. 5) which was inspired in the stretched exponential proposed by K. To (2005) and D. Durian (Thomas and Durian 2015).

$$P_c = (a + bv)^{-(R/d_p)^2} \quad (5)$$

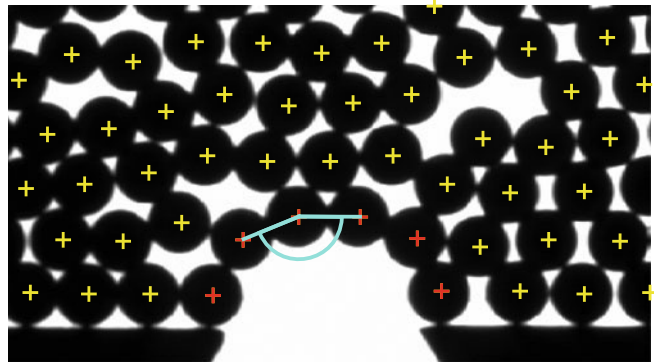
Remarkably, this new expression included only two fitting parameters to describe all the results obtained when varying both the outlet size and the velocity of the grains. The first parameter (a) accounts for the geometrical effects of clogging and was the only one affecting the value of the probability of clogging in the quasi-static regime, that is, when the velocity of the grains tends to zero. The second (b) accounted for the kinematic effects and enters Eq. 5 as a factor the velocity of the grains v . As the experiment was performed in 2D, the exponent was the rescaled outlet size raised to the power of 2. The authors demonstrated that this expression (with the same fitting values) was also valid to reproduce the data obtained in a standard silo (discharged purely by gravity without a conveyor belt) if the velocity of the grains is replaced by the well-known relationship $v = \sqrt{gR}$ proposed in Beverloo et al. (1961).

Arches

As clogs are caused by the formation of arches, it is natural to study the properties of these mesoscopic structures and try to establish a relationship between them and the macroscopic behavior. For example, it is interesting to establish a connection between the microscopic properties of the particles conforming the arch, and its shape or stability. We will now approach the topic of the arch shape and its relationship to clogging.

A natural way to describe the arch shape is through the angles subtended between the centers of consecutive beads (Fig. 15): the center of every

Statistical Mechanics of Clogging, Fig. 15 Photograph of a clogging arch in a flat bottomed 2D silo. The angle formed by the centers of three beads is defined as ϕ . (Reprinted from Lozano et al. (2012b))



three beads in contact subtends an angle ϕ , and therefore the set $\{\phi_i\}$ is a straightforward way to define the shape of an arch blocking the exit orifice. In the model of To (see Fig. 4, right) these angles must be smaller than 180° (To et al. 2001). This is a good approximation because most of the beads indeed fulfill this condition, and if friction is very small this should hold. Nevertheless, in experiments it is found that angles can be higher than 180° , meaning that the beads associated to that angle are hanging from the neighbors due to friction. In one particular realization using a flat bottomed hopper it was found that the proportion of such beads was as high as 17% (Garcimartín et al. 2010). They were called defects, and it can be surmised that they will be rather unstable against perturbations. Although in principle this result would contradict To's ideas, it turns out that the model is quite representative of the real behavior. The reason is that successive angles are anticorrelated (Garcimartín et al. 2010), meaning that a big angle is likely to be found before a small one, and vice versa. Therefore if angles are taken in pairs the average is very likely below 180° , as assumed by the model of To. Finally, let us note that particle shape and friction are paramount in determining how large the angles can be. As reported in To's article of 2001 enhanced friction, as achieved with dented disks, largely increased clogging probability. In particles with flat faces, this effect is exacerbated (Ahmadi and Hosseini 2018; Goldberg et al. 2018).

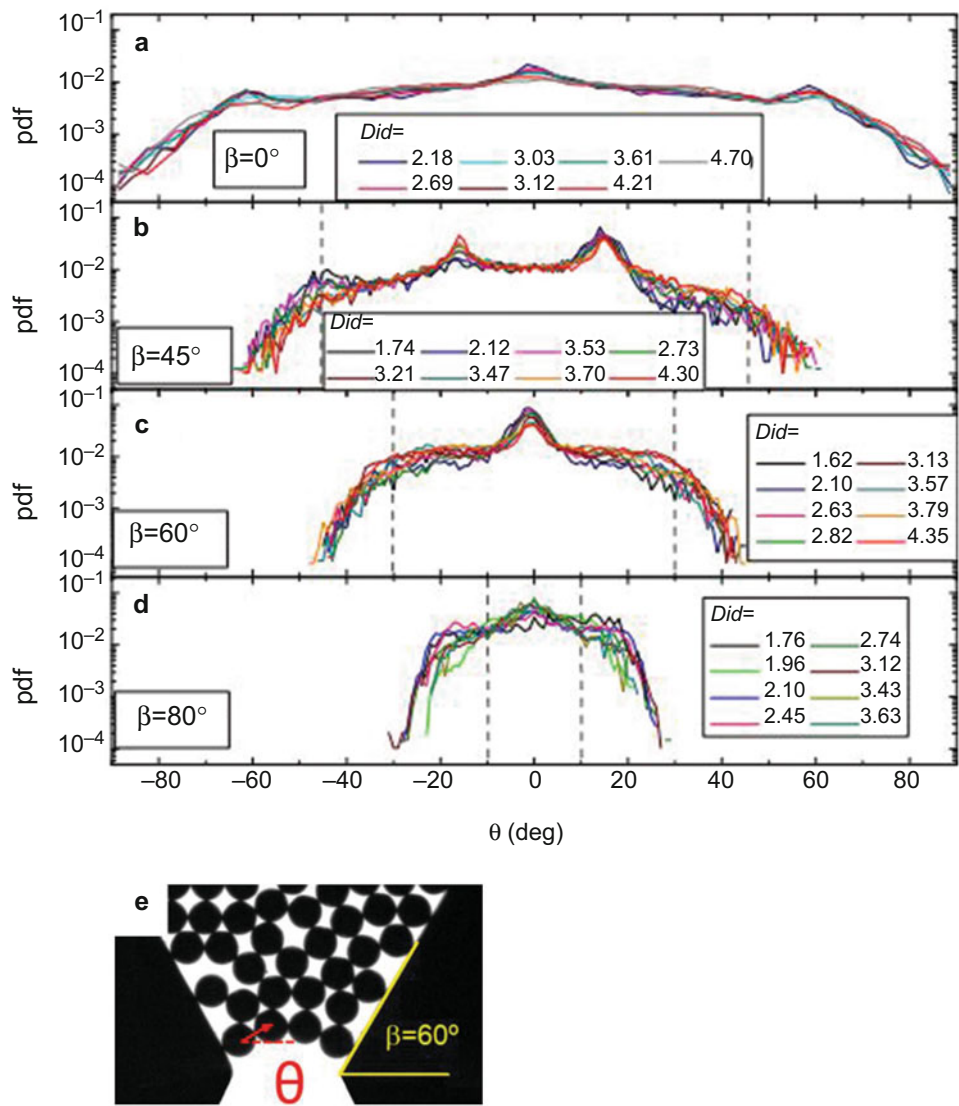
If a hopper is considered instead of a flat-bottomed silo, then the hopper angle introduces

a boundary constraint that determines the maximum values of the angles θ between the segment joining the centers of two consecutive particles and the horizontal (see Fig. 16e). López and coworkers (2019) proposed that for hypothetically frictionless particles in a hopper having an angle β with respect to the horizontal, the angle θ_1 formed by the first two particles (starting from the left) would necessarily be smaller or equal to $(90^\circ - \beta)$. Otherwise, the first particle would be unstable. Then, following To's idea (To et al. 2001), the second angle θ_2 should be equal or smaller than θ_1 , and so forth, until the last one θ_{n-1} , which must fulfill the condition of being larger than $-(90^\circ - \beta)$. Therefore, all the angles θ should fall within a range determined by the hopper angle as denoted by the following equation:

$$\begin{aligned} (90^\circ - \beta) &\geq \theta_1 \geq \theta_2 \geq \dots \geq \theta_{n-1} \\ &\geq -(90^\circ - \beta) \end{aligned} \quad (6)$$

Experimental results are in good agreement with this interpretation (see Fig. 16), although some values of θ are also observed beyond these limits, a behavior that was attributed to friction.

As a consequence of the restriction of possible angles provoked by the hopper walls, it happens that the number of allowed arches is drastically reduced as the hopper angle increases. Consequently, the clogging probability diminishes. Besides, for large hopper angles, the narrow range of angles allowed (see Fig. 16d) imposes that arches are almost flat; as a consequence, the number of beads in the arch becomes discretized



Statistical Mechanics of Clogging, Fig. 16 (a–d) Probability distribution function of the angle θ between the centers of two consecutive particles in an arch and the horizontal, as indicated in (e). β is the angle that the hopper makes with the horizontal. In a–d the curves represent

and the clogging probability changes stepwise with the size of the exit orifice. This contrasts with the case of a flat bottomed silo, where the distributions are rather wide (see Fig. 16a). In this case, it was shown that the arches display a wide variety of shapes, although they tend to be semi-circular when the outlet size was enlarged (Garcimartín et al. 2010).

values of θ obtained for different outlet sizes (as indicated in the legend), and the vertical dashed lines, the limit values that would be imposed by the hopper walls for a frictionless sample. (Reprinted from López-Rodríguez et al. (2019))

An interesting question in relation with the arch shape concerns their connection with the forces that they withstand. This relationship can only be statistical: it is impossible to establish a univocal correspondence between shape and force, as one arch shape can tally with many different force distributions. In two dimensions, Valdes and Santamarina (2008) pointed out that

the mean force orientation in the packing would determine the optimal arch shape: for vertical and horizontal average forces, the optimal shape is parabolic or a catenary; and for a uniform force orientation distribution, the optimal shape is semicircular. In fact, the semicircular shape observed for large arches in Garcimartín et al. (2010) was attributed to a uniform orientation of the forces within the silo. Although arches are not necessarily an optimal response to the orientation distribution of forces, this result can be taken as a hint, showing how shape can provide valuable information about the forces.

Unfortunately, the measurement of the forces at the grain level is not easy (Daniels et al. 2017) and, as far as we know, it has been never systematically performed for clogging arches. Therefore, all the knowledge we have about this topic comes from numerical simulations, as in the work of Pugnali and collaborators (2006) where the forces in the arches developed within a column of grains were analyzed. Forces in clogging arches have been investigated in Hidalgo et al. (2013) and Longjas et al. (2009). Indeed, in Longjas et al. (2009) the forces were used to infer the proportion of possible arches that would be stable and, therefore, able to cause clogging. However, this analysis was limited to arches of three particles. In a subsequent work (Hidalgo et al. 2013), molecular dynamics simulations were used to unveil that the normal forces within the particles conforming the arch are, in average, much larger than the ones among particles in the bulk. In addition, an important relation among the angle subtended among every three particles ϕ and the average force was observed: the larger the angle, the higher the tangential, and the lower the normal force. Therefore, the higher the angle, the higher the friction mobilized to sustain the particle. This result is consistent with experimental data reported in the following chapter concerning the resistance of arches against perturbations.

Unclogging

Once an arch that blocks the orifice is formed, in principle it will last forever. The formation of an

arch involves a mechanically stable configuration, and therefore a perturbation is needed to break it. This may come in different forms. Thermal cycles, for instance, may make the grains dilate and contract, hereby disturbing the contact forces. Although this method has not been used specifically to unclog a silo, it was shown that this procedure can compact a granular medium, which is closely related to breaking arches inside it (Divoux et al. 2008). Local perturbations on the grains at the orifice, for instance with a fluid jet (Zuriguél et al. 2005), or a movable orifice (either oscillating (To and Tai 2017) or rotating (To et al. 2019)) have also been used. However, an external vibration is probably the most extended method to restore flow when an orifice clogs; this is especially true in industry and applications, where silos and hoppers with the addition of a vibrating mechanism are often used. Indeed, vibrations can be also coupled to air injection to fluidize granular materials stored in industrial silos, especially of cohesive grains (Wes et al. 1990). Finally, the vibration of lateral walls as a means of enhancing the flow has been also proved to be a good alternative (Pacheco-Martinez et al. 2008).

Among all these ways to disturb the clogging arches and resume the flow, we will focus here on vertical vibrations applied to the silo bottom or to the whole silo. The reason is that this situation allows for a relatively easy way to quantify the strength of the external perturbation introduced. As a matter of fact, a silo submitted to a sinusoidal vibration of frequency f and amplitude A is relatively easy to implement in the laboratory. Importantly, it has been shown (Wassgren et al. 2002) that the flow rate of a vibrated silo does not change drastically with respect to a static one, provided that the amplitude is small and the frequency is higher than the characteristic time of the dynamics (Chen et al. 2006; Evesque and Meftah 1993; Mankoc et al. 2009; Suzuki et al. 1968). This allows a straightforward comparison of vibrated and static silos. Indeed, in a vibrated silo with a small orifice it was shown an intermittent flow in which the distribution of flow intervals follows an exponential distribution (Mankoc et al. 2009). As explained in section “Clogging as a Stochastic Process” for the avalanche size distribution, this

means that the probability of clogging is constant along time, and that clogging events are uncorrelated. Therefore a single characteristic time can describe this process, which can be related to the mean flowing time, the clogging probability of a single bead as it passes through the orifice, and the avalanche size. On the contrary, the distribution of clogging intervals revealed wider tails. Notably, the same scenario was found for horizontal vibrations of the orifice (To and Tai 2017).

The nature and specific properties of these tails were studied more closely by Janda et al. (2009b). Although the research was aimed to obtain a delivery device that could release a small quantity of grains in a controlled fashion (and thus some of the experiment details, such as the orifice shape and the vibration mechanism, were highly specific), similar features to the results reported in Mankoc et al. (2009) were observed concerning the dynamics of clogging and unclogging. Again, the flowing intervals were shown to be distributed exponentially, while the duration of clogs was suggested to follow a power law: $\text{pdf}(T_J) \propto T_J^{-\alpha}$ (Fig. 17). This implies the absence of a characteristic time scale for the clog duration, and then, it follows that the probability that a clogging arch is shattered is not constant along time. Remarkably, it was found that for some specific values of the variables, the exponent α of the power law was lower than 2, implying that the average clog

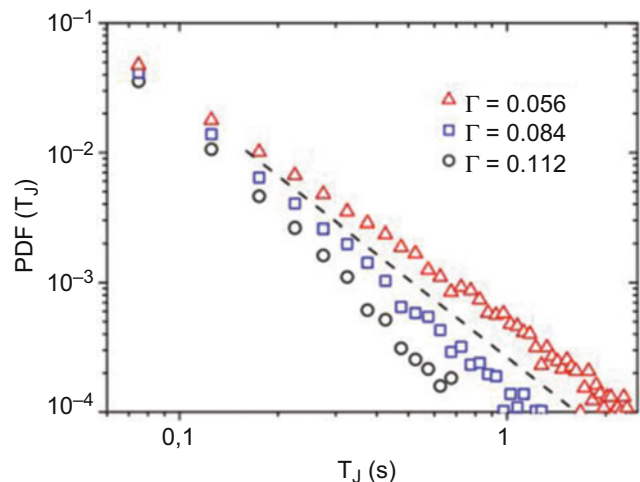
duration (calculated with an integral including the probability density function) does not converge. All these facts hint that the process of breaking arches with vibrations involves complex dynamics.

In order to explore how the clogging arches are broken, two broad kind of procedures can be used concerning the kind of vibration applied: either a vibration of growing amplitude (a ramp), or a constant amplitude vibration. In the first case, the intensity of the perturbation grows along time, which is a natural way to probe the force, or acceleration, that arches can withstand. On the second case, the time that arches last under an imposed perturbation is studied. The next two sections are devoted to explain the investigations related to these different approaches.

The Weakest Link

In order to test the endurance of arches, the idea is to place a silo on top of a shaker and, when an arch is formed, to start a vibration ramp at a constant frequency and a linearly growing amplitude (Lozano et al. 2012b, 2015). Then, the instant when the arch is broken can be measured, and hence the acceleration needed to break it. In addition, if the silo is two-dimensional, the shape of the arch above the orifice can be monitored. As the variable considered here is the force needed to break the arch, the adimensional parameter $\Gamma = \frac{A\omega^2}{g}$ is used to quantify the vibration, which

Statistical Mechanics of Clogging, Fig. 17 Log-log plot of the pdf of the time lapses during which the flow is arrested using an inclined hopper with an aperture of around $R = 1.78$ times the particle size. The dashed line has a slope of two so the slope of the distribution for lowest acceleration Γ (see legend) is smaller than this value. (Reprinted from Janda et al. (2009b))



is the maximum acceleration in gravity units (ω is the angular frequency).

The first remarkable result obtained with this protocol is that the shape of the arch is closely related to the acceleration needed to break it (Lozano et al. 2012b). In particular, if we focus on the angles subtended between the centers of adjacent beads (ϕ), then arches having beads with an associated angle larger than 180° (or, *defects*) are the weakest. Indeed, it was found that the larger the maximum angle in an arch ($\phi_{\max}$), the lower the acceleration needed to break it (Fig. 18). Although this is only true in a statistical sense, a linear fit between Γ and $\phi_{\max}$ was proposed for $\phi_{\max} > 180^\circ$: $\Gamma = -C_1(\phi - 80^\circ) + C_2$, where C_1 and C_2 are positive constants that depend on the friction coefficient. This relationship holds for materials with different friction coefficients. By extrapolating the curve, a limit value of $\phi_{\max}$ close to 200° was found for steel beads (the exact value depends on the material). Interestingly, the distribution of ϕ revealed an abrupt decrease at an angle around 200° . Therefore, this figure was interpreted as a cut-off value above which particles cannot be sustained by frictional forces anymore. A simple model was proposed to account for the relationship between Γ and $\phi_{\max}$ explained above.

As a general result, it was concluded that the bead with $\phi_{\max}$ was the weakest link in the arch, especially if that angle was bigger than 180° . Apart from the dependence of the arch robustness on $\phi_{\max}$ explained above, it was also evidenced that

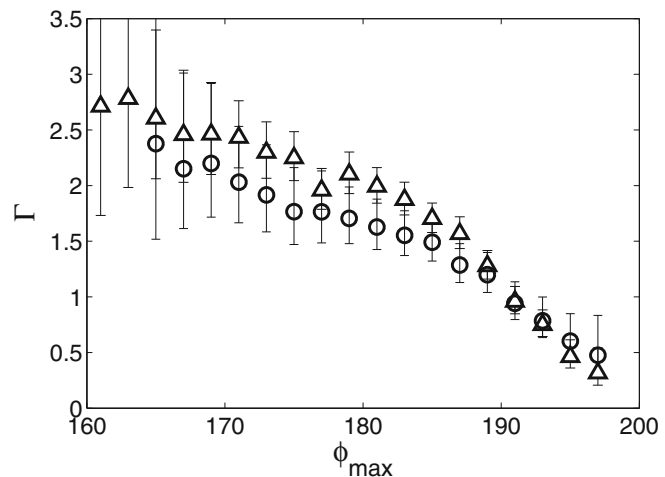
the likelihood of the arch breaking precisely at that defect was bigger than in other positions. Then, in a subsequent work (Lozano et al. 2015) these findings were generalized to other acceleration ramps, and several outlet sizes. In particular, it was found that even comparing sets of arches with the same maximum angle, the ones corresponding to larger outlet sizes displayed lower values of Γ , indicating that $\phi_{\max}$ is not the only variable determining the stability of the clogging arch.

Arch Breaking Is a History Dependent Process

An alternative approach to study the arch breaking process is to apply a constant vibration and measure the breaking time (or, the time it takes for the vibration to shatter the arch and restore the flow). This is analogous to the procedure explained at the beginning of this chapter as implemented in (Janda et al. 2009b; Mankoc et al. 2009). However, in the cases that will be described below, the external excitation was not acting all the time but was started after the formation of a clogging arch that was formed without vibration. With this procedure, it is guaranteed that the arches formed are not broken by the impacts of particles coming from above, or in other words, by the intrinsic noise within the silo before all the kinetic energy is dissipated.

Results of such an experiment were reported in (Zuriguel et al. 2014) where risk analysis was used to describe the time that arches can resist a constant vibration. Let us call t_b the time it takes to

Statistical Mechanics of Clogging, Fig. 18 The average maximum acceleration Γ at the instant of arch breaking, as a function of $\phi_{\max}$, the maximum angle in the arch. Triangles and circles correspond to steel and brass beads respectively. Error bars are 95% confidence intervals. (Reprinted from Lozano et al. (2012b))



break an arch. Then, the survival function S at time t is defined as the probability that an arch lasts more than t . Mathematically,

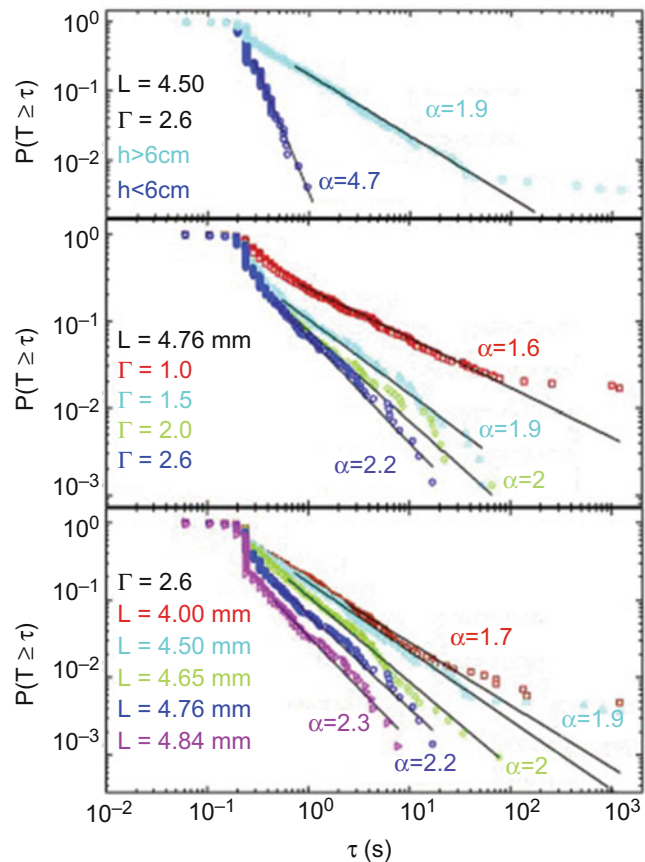
$$S(t) \equiv P(t_b > t) = \int_t^{\infty} P(t') dt' \quad (7)$$

where $P(t)$ is the probability distribution function, or pdf, of t_b . Note that if $P(t) \sim t^{-\alpha}$, then $S(t) \sim t^{-\alpha+1}$. Observations are robust in finding heavy tails (see Fig. 19), meaning that for times larger than a given value ($t_{\text{threshold}}$) S decays as a power law. As stated before, this indicates that the probability of breaking an arch is not constant along time. Moreover, it was confirmed that in some cases the exponent α is such that the integral does not converge. In particular, the role of three parameters on the distribution of breaking times was explored in Zuriguel et al. (2014). It was shown that increasing the outlet size or the intensity of vibration leads to a

bigger α , whereas an increase of the number of grains above the clogging arch implied a reduction of the exponent. It was also demonstrated that distributions for which the average diverges ($\alpha \leq 2$) took place for low vibration intensities, small orifices, and large heights of the column of grains above the clogging arch (Fig. 19).

In addition, the distributions of Fig. 19 reveal that in some cases the curves flatten for very large times (typically above 100 s). Overall, the trends displayed by the survival functions hint to the following interpretation. When a constant vibration is imposed, some arches break down in a relatively short time (say, a few tenths of seconds). After this time ($t_{\text{threshold}}$), surviving arches are harder and harder to break, so the breaking time for these arches lacks any characteristic scale. In this temporal range $S(t)$ is compatible with a power law decay. Finally, it seems that there are a few arches that are even more enduring, so the

Statistical Mechanics of Clogging, Fig. 19 Clogging time distributions in a two-dimensional silo. (Top) Time lapse complementary CDFs obtained using $L = 4.50$ and $\Gamma = 0.26$ for two different heads of grains above the silo bottom ($h < 6$ cm and $h > 6$ cm). (Middle) Time lapse complementary CDFs obtained for $h > 6$ cm, $L = 4.76$ and several Γ as indicated in the legend. (Bottom) Time lapse complementary CDFs obtained for $h > 6$ cm, $\Gamma = 0.26$, and several outlet sizes as indicated in the legend. (Reprinted from Zuriguel et al. (2014))

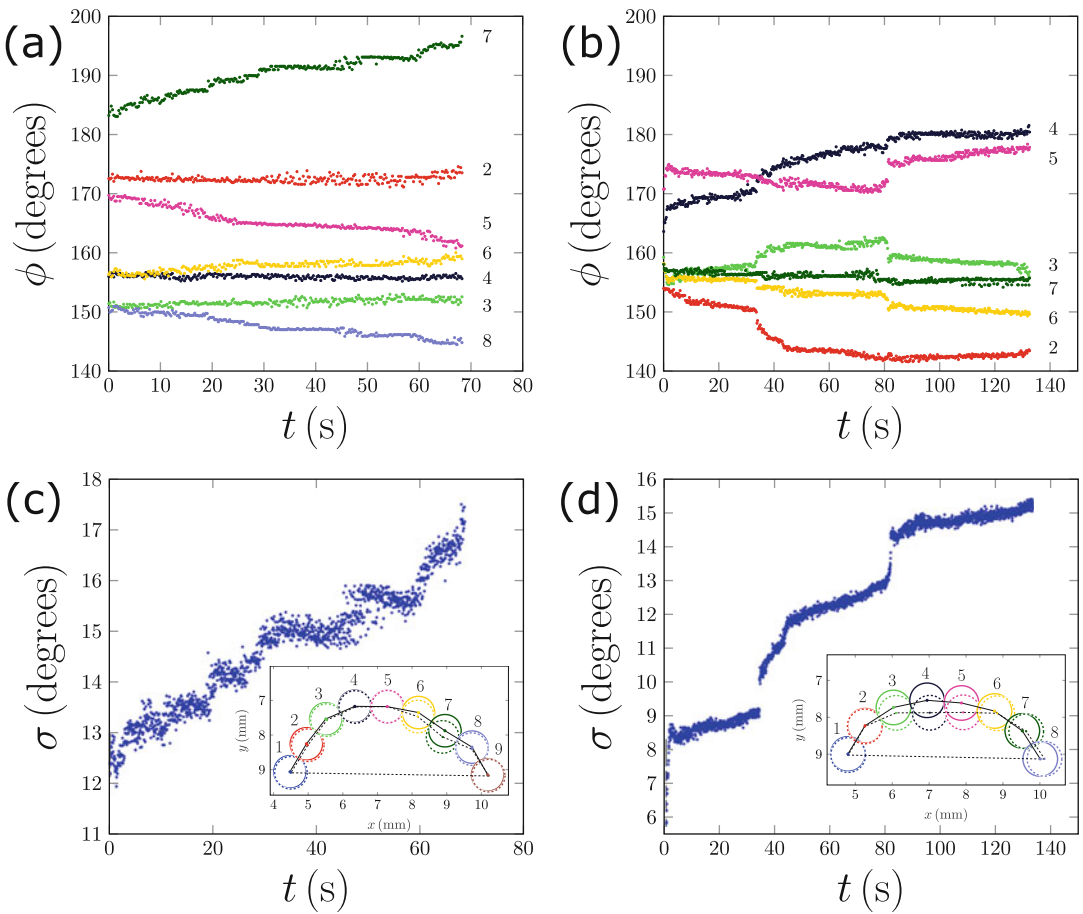


vibration seems unable to break them, and cause a final flattening of the distribution. This latter result was confirmed in Lozano et al. (2015) where for some of experimental conditions the distribution almost completely flattened after a time of about 50 to 100 s, suggesting that there are some arches that the vibration cannot break for the parameter range explored.

In order to unveil the origin of the broad tails of the breaking times distributions and the final flattening, Guerrero et al. analyzed the movements of individual beads in an arch along time prior to their collapse (Guerrero et al. 2018). They observed that under a gentle, constant vibration,

the beads hardly move except for fast rearrangements (fast meaning that they take place in a short time compared to the life of the arch). This can be observed by plotting the temporal evolution of the values of $\{\phi_i\}$ for all the beads in the arch. Alternatively, one can use a single number: σ (the standard deviation of all the values ϕ_i found in a given arch) which captures the rearrangements of the arch as illustrated in Fig. 20.

A key feature that can be deduced from these time series is that the angle rate of change is not proportional to the angle itself. From experiments with a vibration ramp one could have naively



Statistical Mechanics of Clogging, Fig. 20 Evolution of two different long-lasting broken arches, (a) plus (c), and (b) plus (d). Upper panels show $\phi(t)$ for each grain. The lower panels show σ (the standard deviation of all the values ϕ_i found in a given arch). The color and the number

on the right side of each $\phi(t)$ curve indicate the bead of the arch (see the insets in lower figures). The inset shows the position of each bead of the arch at two instants: just after starting the vibration (solid line) and just before the collapse (dashed line). Reprinted from Guerrero et al. (2018)

expected that at least the bead associated to the biggest angle (the most dangerous one) would evolve in such a way that its angle would monotonously grow until it reached the point of collapse. This is not the case if the arch is submitted to a gentle, constant vibration. The evolution of individual angles is much more complex than that.

In order to analyze the slow relaxation dynamics, one can calculate the two time autocorrelation function of σ , for a lag time τ and a waiting time t_w :

$$C(t_w, \tau) = \frac{\langle \sigma(t_w + \tau) \sigma(t_w) \rangle - \langle \sigma(t_w + \tau) \rangle \langle \sigma(t_w) \rangle}{\sqrt{\text{VAR}(\sigma(t_w)) \text{VAR}(\sigma(t_w + \tau))}} \quad (8)$$

where $\langle \dots \rangle$ denotes the ensemble average. It was found that the correlation decreases with τ ; but notably, it also depends on t_w , denoting that the process is not stationary along time. For long waiting times, C tends to a limit value. It had been pointed out (Nicodemi and Coniglio 1999) that aging effects often show a logarithmic dependence on this time, and this was precisely the behavior observed for the dependence of C on t_w for a fixed τ .

Aging is a nonergodic process in which the ensemble average and the time average are not equivalent. Some models have been proposed to explain the behavior of these arches. Nicolas and coworkers (2018) considered that the arch being vibrated is able to explore an energy landscape in which traps represent more stable configurations. Using a simple shape for the energy wells and the escape rate proposed by H. Kramers (1940), a survival function that reproduces the basic features of the experimental observations was obtained. Also, in an effort to understand nonergodicity, C. Merrigan and coworkers (2018) rationalized the intermittent motion of the beads as a continuous time random walk of a vector whose components are the angles $\{\phi_i\}$ of the arch. They simulated vibrated arches and noted how this model is consistent with ergodicity breaking. They went on to compare some of the numerical results with experiments, finding an overall good agreement, notwithstanding several discrepancies (Guerrero

et al. 2019). The notion of the arch performing a random walk in the space of locally stable arch shapes, where each shape is characterized by a dwelling time that depends on the depth of the trap, is therefore quite reasonable.

Summary and Discussion

Along this work we have summarized the existing knowledge about clogging of macroscopic inert particles when passing through a constriction. The typical instance of this scenario is the discharge of a silo through a small orifice, a system in which it is well accepted that the development of clogging can be described as a Poisson process. The reason behind this is that the emergence of a clog is equally likely at any time during the discharge. In practice, this feature is typically inferred from the statistics of the avalanche sizes which, in all cases but in narrow slits, reveal an exponential tail. This implies that the mean avalanche size (as well as the mean avalanche duration or the probability of clogging) is always well defined.

As a matter of fact, for its simplicity and easiness to obtain, the avalanche size is often used to characterize the effect of different variables on clogging development. Among these variables, the most influential is clearly the outlet size (or more precisely, the ratio between the outlet and particles size). Indeed, it is known that the mean avalanche size abruptly grows when this parameter is increased. The question about the existence of a critical outlet size above which clogging is not possible is still open, although mounting evidences suggest that the clogging transition is similar to the glass and jamming ones. In these cases, relaxation times grow dramatically but do not necessarily imply the existence of a critical point.

Concerning other parameters that affect clogging, we have underlined the role of two: the volume fraction and the velocity of the grains at (or near) the orifice. The former is a contributing factor, as it determines the probability that a given number of grains coincide above the outlet and form an arch. The latter, however, has been argued to affect the number of these arches that are able to

become stabilized and survive after all the kinetic energy within the system is dissipated. Then, the higher the velocity of the grains, the smaller the number of arches that are stable, and therefore the lower the probability of clogging. Interestingly, the reason for which a suitably placed obstacle above the orifice is able to dramatically reduce the clogging probability can be associated to an alteration of these two parameters: the obstacle reduces the pressure, confinement and packing fraction near the orifice (so it prevents arch formation), and besides, it alters the velocity field increasing the kinetic energy of the grains at the outlet (so it prevents arch stabilization).

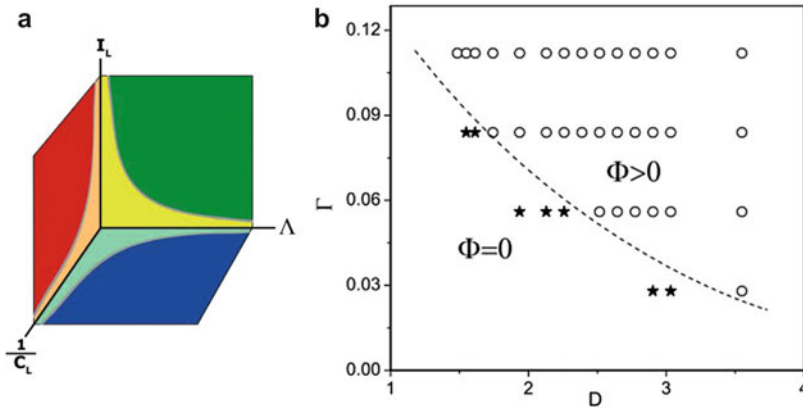
Once a clog is formed, an external input of energy is necessary to resume the flow. The most widely employed method to perform this task is to apply a vibration (either locally at the exit, or to the whole silo). For low intensity vibrations, it has been reported that the distributions of breaking times (i.e., the time that takes since the vibration is applied until the collapse of the arch) display fat tails. These tails can be fitted to power laws, whose exponents depend on different parameters such as the intensity of vibration, the outlet size, and the height of the layer of grains within the silo. It has been remarked that in some cases, the exponent of the power law is smaller than two, a feature implying that the first moment of the distribution cannot be calculated as the integration does not converge.

It is noteworthy that the different nature of the flowing and the clogging times – the former being an exponential distribution, and the latter displaying a power law tail – has also been observed in the passage through bottlenecks of other discrete systems. In particular, it was experimentally shown (Zuriguel et al. 2014) that the flow of sheep through narrow doors displayed an intermittency that could be described within this framework. Moreover, in this scenario, the distribution of clogging times when placing an obstacle in front of the door revealed an exponent higher than obtained in a standard entrance (without obstacle); this implies a beneficial effect of the obstacle as it reduces the number of long lasting clogs. In the same work, simplistic simulations of

pedestrian evacuations through a bottleneck also showed how reducing the desired speed of the agents (which in a congested scenario amounts to diminishing the driving force) lead to an augment of the power law exponent, improving the flow. The same effect was reached when increasing the outlet size or the intrinsic noise included in the movement of these bodies. Finally, in a simulated colloidal suspension, it was also observed an augment of the exponent when increasing the bath temperature.

Considering all these outcomes, a phase diagram of sorts was proposed to account for the clogging behavior in different systems of solid particles flowing through bottle-necks (Zuriguel et al. 2014). The order parameter introduced was $\Phi = \frac{\langle t_f \rangle}{\langle t_c \rangle + \langle t_f \rangle}$ where $\langle t_f \rangle$ is the average duration of the flow intervals and $\langle t_c \rangle$ is the average clog duration. As $\langle t_c \rangle$ only converges when the exponent α of the power law is larger than two, $\alpha \leq 2$ implies $\Phi = 0$; a feature that was proposed to qualify the “clogged state.” On the contrary, when $\Phi > 0$ it can be said the system is in an “unclogged state.” In the latter scenario, the flow can be either continuous if $\Phi = 1$, or intermittent if $0 < \Phi < 1$. From this, the effect of the different variables in the values of Φ was tested, checking that the system could reach the clogged state (i.e., $\Phi = 0$) by decreasing the exit size and reducing the particle’s excitation (intrinsic or external). Also, augmenting the pressure at the narrowing seemed to drive the system to a clogged state. According to these findings, and inspired along the concepts of compatible and incompatible load introduced by Cates et al. at the end of the last century (Cates et al. 1998), all the variables affecting clogging were encompassed in three general magnitudes: the characteristic size of the neck (λ), the incompatible load (I_L) and the compatible load (C_L) as depicted in Fig. 21 (left). For the case of a vibrated silo, a more detailed phase diagram for the plane $\Gamma - D$ (which in the framework of the generic variables corresponds to the plane $I_L - \lambda$) was reported in Zuriguel et al. (2017) (see Fig. 21, right).

In recent years, several lines of investigation have reported a number of results which are



Statistical Mechanics of Clogging, Fig. 21 Left, generic phase diagram proposed for the flow of many-particle systems through bottlenecks. Right, phase diagram for the plane $\Gamma - D$ obtained for the locally vibrated eccentrically discharged hopper used in (Janda et al. 2009b). Stars indicate points where $\Phi = 0$ (clogged

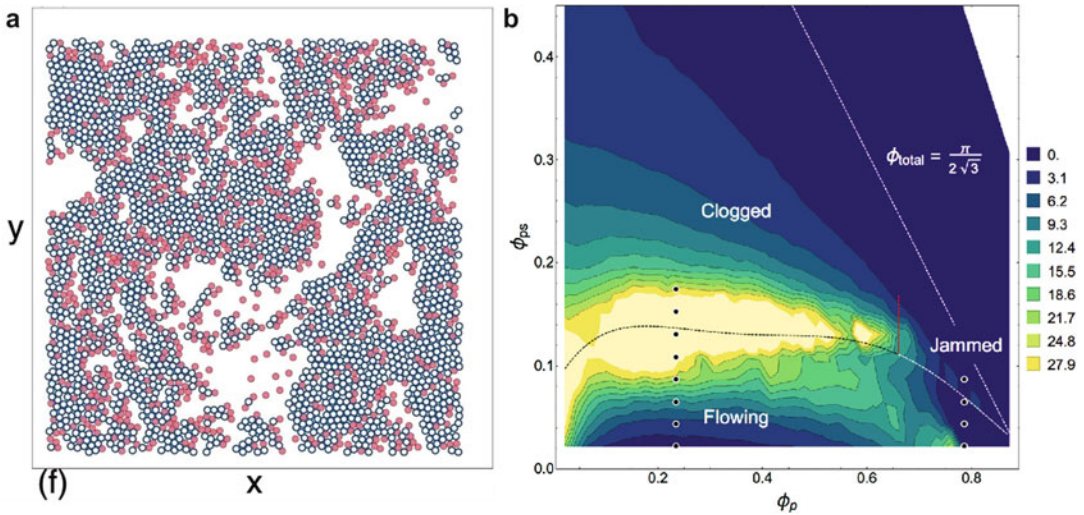
phase) and circles show positions where $\Phi > 0$ (unclogged phase). The dashed line is a guide to the eye suggesting a possible boundary between the two phases. (Reprinted from (Zuriguel et al. 2014) (left) and (Zuriguel et al. 2017) (right))

congruent with the proposed global framework. For example, real pedestrian drills evidenced that the stronger the force applied by the crowd in their way out of a room, the slower the evacuation (which can be considered as a slightly modified version of the traditional Faster is Slower phenomenon in pedestrian dynamics) (Pastor et al. 2015). The reason behind this behavior was on the increment of the clogging times with a higher force (compatible load). Also, it seems that the increment of the compatible load was behind the transition from unclogged to clogged states reported for the flow of small robots (Vibration-Driven Vehicles) when passing through a narrowing (Patterson et al. 2017). In that case, instead of altering the force of each individual, the increment of the compatible load was achieved by increasing the number of agents inside the room.

Apart from the interest of the phase diagram from the point of view of clogging, its resemblance to the scheme introduced for the jamming transition by Liu and Nagel (1998) has stimulated recent investigations on the relation among these two states. In principle, clogging and jamming are two well-differentiated phenomena: clogging is a local occurrence triggered by the formation of a mesoscopic structure (an arch) that is able to arrest

the grains (or bodies) behind it; on the contrary, jamming is a global state of the matter where different kind of spatially averaged quantities can be measured and used to characterize the system response.

Recently, Reichhardt and collaborators have started to investigate the connection between these two phenomena (Nguyen et al. 2017; Péter et al. 2018). To this end, they have developed numerical simulations of the flow of particles through arrays of obstacles, implemented as pinned particles (see Fig. 22, left). Then, depending on the number of pinned and mobile particles, the system was found to reach different stationary states: fluid, clogged, or jammed, as illustrated in Fig. 22 (right). Remarkably, the clogging transition was reported to have characteristics of an absorbing phase transition in which, after a transient time, the system evolves into a heterogeneous state as the one represented in Fig. 22 (left). This transient time was shown to diverge at the transition as illustrated by the yellow region in Fig. 22 (right). In contrast, jamming was proved to be a rapid process in which the sample does not reveal any sign of heterogeneity. In this case, the magnitude that diverges as the jamming density is approached turns out to be the rigidity.



Statistical Mechanics of Clogging, Fig. 22 Left: Final clogged state of mobile disks (blue open circles) driven in the positive x direction through obstacles (red filled circles) in a sample with obstacle density $\phi_{obs} = 0.175$ and disk density $\phi_m = 0.436$. Right: Map of the transient times τ obtained depending on ϕ_{obs} vs ϕ_m . Yellow corresponds to large τ and blue to small τ as indicated in the legend. The

dark dashed line is a guide to the eye marking the crossover from a flowing state to a clogged state, while the white dashed line indicates the transition from a flowing state to a jammed state. In the white region, there are not data as it is above the maximum density that could be reached in the implemented model. (Reprinted from Péter et al. (2018))

All these results – which are similar to the ones reported in a previous work of Tejada et al. (2016) – have been partially confirmed by Stoop and Tierno in experiments where they drove colloidal monolayers across different arrays of obstacles (Stoop and Tierno 2018). Remarkably, in the experimental conditions implemented in this research, the Faster is Slower effect –characteristic of the flow through bottlenecks of pedestrians – was also identified. Again, this is another evidence that supports the existing connections on the behavior of different many-body systems when flowing through constrictions.

Future Directions

Although the amount of knowledge gained in the last two decades on the silo clogging problem is rather considerable, it is also true that the number of questions that are still unanswered is also numerous. Here, we are going to indicate some of the problems we consider more stimulating, either from a fundamental or by an applied point of view.

First, it will be interesting to deepen in the relationship among clogging and jamming. As mentioned above, this topic has been approached within the framework of a simulation where a dense sample of mobile particles flows through a series of obstacles. Although the findings of these simulations have been somehow validated by experiments with colloidal suspensions, it would be nice to see if the same behavior can be experimentally tested using dry macroscopic grains. Also, there are some other systems which may help to shed light on this jamming-clogging connection. One of these is the flow of inert grains through very narrow pipes. In this geometrical configuration, it has been recently shown that clogging is also possible due to the development of hanging arches supported by frictional forces against the wall (Janda et al. 2015; Verbücheln et al. 2015). As in this pipe flow there is not a bottleneck that introduces a local inhomogeneity, it is possible that the conditions leading to clogging are comparable to the ones leading to jamming. In addition, the study of clogging in narrow vertical pipes is of great applied interest as the formation of hang-ups is one of the major

problems in ore transportation in underground mining (Hadjigeorgiou and Stacey 2013).

Another issue that should be carefully investigated in the forthcoming years is the parallels among clogging in 2D and 3D scenarios. Although most of the features observed in relation with clogging are similar in two and three dimensions, some differences exist. The most salient one concerns the divergence of the mean avalanche size with the outlet size, which seems to take place in 3D silos but has been practically discarded in 2D ones. In addition, the statistical analysis of the properties of arches and the effect of different variables (such as the hopper angle) has been mostly approached using 2D silos, so an extension to 3D scenarios is needed. This could be tackled by studying the role played by the silo thickness in quasi-two-dimensional geometries, gradually changing from a 2D silo formed by a monolayer of grains to a fully 3D case.

Considering the role of all the different variables summarized in this work, it seems that investigating the effect of combining more than one of these parameters can be fruitful to better understand the physical mechanism behind clogging. For example, knowing the dramatic augment of the probability of clogging occurring when the grains flow through the outlet in a quasi-static manner, it would be interesting to see if in this regime the effect of geometrical aspects (such as the hopper angle or the placement of an obstacle) is similar to the one observed in conditions of free discharge. In this way we will be able to ascertain if the role of these variables is due to its effect on the geometrical or dynamical aspects. Also, further investigation in the configuration where the grains are extracted by an external device (a belt or an endless screw) is important because this is a common procedure in industry.

Doubtless, more investigations are needed in other systems that could also display clogging, such as active matter or pedestrian dynamics. Of course, this research is not straightforward given the complex nature of the agents involved in these fields and the intrinsic difficulty associated to performing experiments at the micro scale or with pedestrians. Nevertheless, other systems such as macroscopic active materials (or small

robots) can be reasonable models in which to incorporate some intrinsic activity to the particles and compare with the behavior of inert granular media. Similar reasoning holds for very promising studies of submerged grains (Koivisto and Durian 2017) and suspended particles (Guariguata et al. 2012; Lafond et al. 2013; Marin et al. 2018), which can be seen as examples with a behavior that is halfway between granular materials and colloidal suspensions.

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Jamming of Granular Matter

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Glossary

Granular matter Material such as sand or sugar, which is composed of independent, macroscopic particles characterized by short range interactions that do not conserve energy. Energy is lost to excitations of internal degrees of freedom, and is then unavailable for macroscopic flow.

Supercooled liquid A liquid cooled below its freezing point by avoiding crystallization.

Shear deformation Deformation of a material in which internal clusters or layers slide past each other.

Couette flow Flow between two surfaces one of which is moving with respect to the other.

Definition of the Subject

A jammed material is defined as one that is structurally disordered but, unlike a fluid, possesses an yield stress. In the field of traditional condensed matter physics, such a material would be called an amorphous solid. The broader use of “jammed” extends this concept to non-traditional materials such as granular systems, foams and colloids. Jamming is, similarly, the extension of the concept of freezing to the transition from a fluid state to a jammed state. Understanding jamming in granular systems is important from technological, environmental, and basic science perspectives. Jamming of grains in silos causes catastrophic failures. Avalanches are examples of unjamming, which we need to understand prevent and control. The phenomenon of jamming in granular matter poses fundamental challenges in basic science because there is no known framework leading from the microscopic, grain level interactions to the macroscopic properties that reflect collective behavior.

Jamming in granular matter is intimately related to stress propagation, and the nature of jamming will depend on whether the material is under shear or isotropic compression. It will also depend on whether there is sustained motion with the grains having a finite kinetic energy or if the system is at rest and being slowly deformed. In the following sections, we explore different types of jamming in granular matter.

Introduction

Experiments point to many similarities between the jamming transition in granular materials (Jaeger et al. 1996a, b; Kadanoff 1999) and other similar non-equilibrium transitions such as that in driven foams, emulsions and gels. The common unifying features are: (a) these are purely non-equilibrium transitions since the flowing state can be

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maintained only by external driving, (b) the systems exhibit anomalously slow dynamics as the transition is approached and (c) there are no obvious structural signatures of the transition. By structural, we refer to the geometric arrangement of particles. In addition, we will see that there is increasing evidence for a divergence in correlation functions for forces in the granular case. Features (b) and (c) are, in fact, similar to a transition in a thermal system; that of a supercooled liquid undergoing the glass transition. The origin of the slow dynamics and the relationship between time and length scales has been studied extensively in the context of the glass transition in supercooled liquids, and it has been shown that the dynamics becomes spatially heterogeneous as the glass transition is approached (Weeks et al. 2000; Donati et al. 1998; Donati et al. 1999; Berthier et al. 2005). There is a time scale and a length scale associated with dynamical heterogeneities and these have been measured in experiments (Berthier et al. 2005) and simulations (Lacevic et al. 2003). Inspired by this framework, dynamical heterogeneities have been explored in experiments on granular systems approaching jamming and a length and time scale associated with the jamming transition has been identified (Keys et al. 2007; Dauchot et al. 2005; Pouliquen 2004).

In granular systems, there is a type of heterogeneity arising from stress transmission which is distinct from the heterogeneity of particle displacements and density fluctuations that are common to both supercooled liquids and granular matter. Stress heterogeneities in flowing granular matter has been studied in experiments on Couette shear flow (Miller et al. 1996; Howell and Behringer 1999; Veje et al. 1999; Geng et al. 2003; Daniels and Behringer 2005a, b, 2006) and in hopper flow (Longhi et al. 2002). Simulations have played a seminal role in the developments leading up to the dynamical heterogeneities framework in supercooled liquids. Likewise, simulations of granular flows can play a role in clarifying the relationship between heterogeneity in different dynamical variables. For instance, a simulation of grains flowing through a hopper (a long, vertical tube with a narrow opening at the bottom), has identified/characterized both stress and displacement heterogeneities.

However, a clear relationship between the two has not been identified (Ferguson and Chakraborty 2007). Indeed, there may be some reason to think that there is anti-correlation between the strong force structures of force chains, and the freedom needed for density fluctuations. Dynamical heterogeneities have been explored in simulations of other types of dense granular flows (Silbert et al. 2002, 2007; Silbert 2005).

The similarities in dynamics between supercooled liquids and granular systems have raised the intriguing possibility of “universality” in the jamming transition. Universality is a concept associated with continuous phase transitions in thermal systems such as the liquid-gas transition or the Curie point in ferromagnets (Chandler 1987). In these systems, universality, owes its origin to the presence of a diverging length-scale at the transition. Microscopic properties of the system can be coarse-grained because of the presence of this diverging length scale and universality classes can be specified by properties such as the symmetry of the system and the spatial dimensionality. These concepts are still evolving in the context of granular systems. However, there are an increasing number of studies that have identified a growing, possibly diverging, length scale.

Statistical Framework of Jamming

The ubiquitous presence of force fluctuations, well-defined statistical distributions and similarities to thermal systems observed in granular systems close to jamming, have led researchers to look for a statistical framework that can describe the spatial and temporal fluctuations in static and quasi-static (weakly driven) granular flows.

Experiments and simulations suggest that the phenomenon of jamming has the flavor of a phase transition. Phase transitions can be broadly divided into two classes: (a) Equilibrium and (b) Non-equilibrium. The former encompasses transitions such as the liquid-solid transition, the superfluid and superconducting transitions, and describes transitions between states which are in thermal equilibrium. Non-equilibrium phase transitions are commonly observed in pattern-forming

systems such as chemical reactions, a well known example being the Belousov–Zhabotinsky reaction (Dolnik et al. 1996), or in fluid flows, such as Raleigh–Bénard convection. The framework of equilibrium statistical mechanics is well established and can be used to analyze and understand equilibrium phase transitions. In contrast, there is no universal framework for non-equilibrium phase transitions even though there are many specific transitions which are well understood (Dhar 2006; Schmittmann and Zia 1995). In many cases where non-equilibrium transitions occur, the systems are locally close to thermal equilibrium, but not globally so. It is then possible to use hydrodynamic-like descriptions involving gradients in relevant quantities, as well as transport models. Transitions in such systems often involve spatially extended modes which become unstable or stable for different control parameters. In the usual case, it is the most unstable mode which dominates, and thermal fluctuations play a very limited role.

An interesting question is whether a statistical approach can be used to understand jamming and other phenomena in granular matter. In such an approach, one would like to know the ensemble of states that are consistent with the external constraints. In the granular case, there is some evidence to suggest that fluctuations are important, particularly near jamming unlike the typical non-equilibrium transition discussed above.

Granular Packings

A static granular packing is in mechanical equilibrium if every grain satisfies the conditions of force and torque balance. At the microscopic level, the grains interact via contact forces, which are frictional. For rigid grains, friction leads to a microscopic indeterminacy of the forces since the tangential force magnitude at a contact has to be *less* than the normal force: $|f_t| \leq \mu f_n$, where μ is the friction coefficient.

There is a broader class of indeterminacy which has to do with the fact that there are many packing configurations that are consistent with a set of macroscopic constraints. For example, if one shakes a box of marbles and examines the positions of the marbles after the shaking has

stopped, the positions and the contact network will be different each time one stops shaking. This is analogous to the situation of systems in thermal equilibrium: many microscopic configurations of the oxygen molecules in a closed room occur while the temperature and total volume remain fixed. Of course, in the granular case, there is no internal ‘shaking’ mechanism.

The different configurations of systems in thermal equilibrium (such as the oxygen molecules in a room) have a given probability of occurring at a given temperature. This probability is well known from equilibrium statistical mechanics and is the Boltzmann distribution: $e^{-\beta E}$. Here $\beta = 1/k_B T$ is the inverse of the temperature T multiplied by the Boltzmann constant k_B , and E is the energy of the configuration. The probability of finding a configuration is, therefore, completely determined by its energy and does not depend on the particular dynamics or the history. This is the essence of systems in thermal equilibrium and leads to their simplicity.

Edward’s Ensemble

The configurations of a box of marbles at the end of a shaking experiment are certainly not in thermal equilibrium. Marbles are large objects, and they dissipate energy as heat when they interact. Ordinary thermal fluctuations are not relevant to a box of marbles; one has to shake them to move them and generate new states. These end states are, however, static. A natural question to ask is whether one can make a priori prediction of the probability of occurrence of a particular configuration, as we can for systems in thermal equilibrium. The first theoretical approach to address this question was that of the Edwards ensemble which asserts that the total volume (V) of a mechanically stable grain packing plays the role of energy, and that there is a temperature-like quantity called the compactivity (Edwards and Blumenfeld 2007; Edwards and Grinev 1999, 2001; Edwards and Oakeshott 1989). The mechanically stable grain packings of infinitely rigid objects have been termed blocked states (Edwards and Grinev 2001), and are related to strictly jammed states (Donev et al. 2004). The basic hypothesis underlying the Edwards ensemble is the microcanonical

(Chandler 1987) hypothesis that all blocked states with the same total volume V are equally likely. This hypothesis has been tested in numerical simulations, in experiments, and in some exactly solvable models (Barrat et al. 2001; Barrat et al. 2000; Coniglio et al. 2001, 2002; Kurchan 2001; Makse and Kurchan 2002). The consensus seems to be that the hypothesis is not universally valid but holds under some conditions. The Edwards hypothesis involves the definition of the Edwards entropy: $S(V) = \ln \Omega(V)$, where $\Omega(V)$ is the density of blocked states, that is, the number of blocked states between V and $V + \delta V$. Evaluating this function has been a challenging problem, although progress has been made recently (Blumenfeld and Edwards 2003).

Force Ensembles

The Edwards picture was originally based on the assumption of completely rigid particles. However, all physical particles have finite stiffness, and in the usual case, interact via frictional contact forces. The conditions of finite vs. infinite stiffness and frictionless vs. frictional interactions has some important consequences for granular packings. Relaxing the infinite stiffness constraint introduces couplings between the positions of grains and the contact forces. Below we discuss an ensemble for frictionless, spherical particles.

A mechanically stable packing of frictionless, deformable, spherical particles have to satisfy the equations of force balance. In addition, there is force law relating the positions of the particles to the forces (Snoeijer et al. 2003a; Tkachenko and Witten 1999). For grains interacting through purely repulsive, short-range, forces, there are dN equations of force balance for N grains in a space of dimensionality d :

$$\text{force - balance} \quad dN \text{ eqs} : \sum_j F_{ij} \frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|} = 0 \quad (1)$$

$$\text{force - law} \quad \langle z \rangle N/2 \text{ eqs} : F_{ij} = f(\mathbf{r}_{ij}) \quad (2)$$

Here $\langle z \rangle$ is the average number of contacts per grain, F_{ij} is the magnitude of the contact force

between grains i and j , the angles of the contacts being fixed by the geometry, and $f(\mathbf{r}_{ij})$ is a function specifying the inter-grain force law. For a given geometry, (i.e. fixed $\frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|}$), the equations of force balance involve $\langle z \rangle N/2$ unknowns. The number of force-balance equations cannot be greater than the number of unknowns, otherwise the forces are overdetermined, and, therefore, $\langle z \rangle N/2 \geq dN$.

For rigid, non-deformable grains, the force law becomes a constraint on the positions of the grains (Tkachenko and Witten 1999). There is one constraint for each contact, which leads to $\langle z \rangle N/2$ equations for the dN positions, the unknowns. Since the number of constraint equations have to be larger than the number of unknowns, $\langle z \rangle N/2 \leq dN$. The force law and the force balance constraints can, therefore be satisfied only if $\langle z \rangle = z_{\text{iso}} = 2d$. This enumeration argument applies only to disordered packings, since for ordered, crystalline packings, angles of the lines connecting the grains are not independent, and therefore, not all the constraint equations are linearly independent. Considering such disordered packings, the enumeration argument leads to the conclusion that packings of rigid, isotropic, frictionless particles have to be *isostatic*; they have to have $\langle z \rangle = z_{\text{iso}}$.

For deformable particles, mechanically stable packings can exist for $\langle z \rangle \geq z_{\text{iso}}$. If the particles are very stiff, the magnitude of the forces change a lot for small changes in the separation between grains. There is, therefore, an effective separation of scales (Snoeijer et al. 2003a, 2004a) in Eqs. (1) and (2), and one can consider the ensemble of forces which satisfy force-balance for a fixed geometry of the packing, i.e., a packing with fixed grain positions. The properties of such force-ensembles have been studied (Snoeijer et al. 2003a, b, 2004a, b, c, 2006; van Eerd et al. 2007), and it has been shown that $P(F)$, the probability distribution function (PDF) of contact forces, evolves to an exponential form as the particles are made increasingly rigid (Snoeijer et al. 2003a; 2004a). In addition, work on sheared and isotropically compressed packings have shown that there are more extended spatial correlations of the forces in the force ensembles for sheared packings (Tighe et al. 2005a).

The force ensemble approach captures many features of packings near Point J. However, the approach to this point involves coupling between the geometry and forces, as observed in simulations (O’Hern et al. 2003). Below, we discuss a generalized ensemble that allows for the coupling of these two, and applies to spherical and non-spherical grains with and without friction.

Generalized Ensembles

In a more recent development, it has been shown that the “equally likely” hypothesis of Edwards and the Microcanonical ensemble of thermal systems (Chandler 1987) is not essential for the definition of a temperature-like quantity, and a much weaker condition of factorizability of distributions is sufficient (Bertin et al. 2004, 2005, 2006). The necessary conditions for being able to define a temperature-like variable and a statistical ensemble based on this variable are (a) the existence of a physical quantity that is conserved by the natural dynamics of the system (in thermal systems energy is conserved but in dissipative granular media, it is not) and (b) that the frequency of finding different states with the same value of the conserved quantity is factorizable: $\omega_{v_1+v_2} = \omega_{v_1} \omega_{v_2}$. The latter condition implies that if one creates a configuration by bringing together two configurations $_1$ and $_2$, then the frequency of occurrence of this joint configuration is a product of the frequency ω_v of the individual configurations.

In the context of mechanically stable packings of grains (soft, deformable or rigid), a conserved quantity that has been identified is the force-moment tensor (Henkes et al. 2007; Blumenfeld 2007; Ball and Blumenfeld 2002) which is related to the Cauchy stress tensor:

$$\hat{\sigma} = (1/V) \sum_{ij} \vec{r}_{ij} \vec{F}_{ij} \quad (3)$$

The summation in Eq. (3) is over all contacts $\{ij\}$ in an assembly of grains, occupying a volume V , with contact vectors $\vec{r}_{ij}$ and contact forces $\vec{F}_{ij}$ (for grains with friction $\vec{F}_{ij}$ does not lie along the direction of $\vec{r}_{ij}$).

The microscopic force moment tensor for a grain is given by:

$$\hat{\kappa}_i = \sum_j \vec{r}_{ij} \vec{F}_{ij}, \quad (4)$$

where the sum is over all grains j that contact grain i . For grains in mechanical equilibrium, it can be shown, using a generalized Stoke’s theorem (Edwards and Blumenfeld 2007; Henkes and Chakraborty 2005, 2008), that the *total* force moment tensor

$$\hat{\Sigma} = \sum_i \hat{\kappa}_i$$

becomes a boundary integral for systems with open boundaries and is a topologically conserved quantity for systems with periodic boundary conditions (Henkes et al. 2007). In two dimensions, this property can be explicitly demonstrated by introducing a set of auxiliary variables (Ball and Blumenfeld 2002) which are the analog of the vector potential in electromagnetism. The connection to electromagnetism is natural if one remembers that for mechanically stable packings, the divergence of the stress tensor is zero, just as the divergence of the magnetic field is zero in electromagnetism.

Given the topologically conserved nature and/or the strict boundary sensitivity of $\hat{\Sigma}$, the phase space of all mechanically stable packings can be grouped into sectors characterized by the value of $\hat{\Sigma}$. Thinking of systems with periodic boundary conditions, the topologically conserved nature implies that packings in different sectors are completely disconnected by any natural dynamics, and therefore, $\hat{\Sigma}$ is the type of conserved quantity that meets criterion (a) of the previous paragraph. If we now assume criterion (b), then a statistical ensemble can be constructed to describe the end states of processes such as shaking grains. The role of energy is played by $\hat{\Sigma}$ which is an extensive quantity (scales with system size) and the analog of temperature is a tensorial quantity, $\hat{\alpha}$ (In the context of infinitely, rigid grains, this intensive variable has been called

Angoricity by Edwards (Edwards and Blumenfeld 2007)). This tensor is defined by:

$$\hat{\alpha}(\hat{\Sigma}) = \frac{\partial Z_0(\hat{\Sigma})}{\partial \hat{\Sigma}} \quad (5)$$

where

$$Z_0(\hat{\Sigma}) = \sum_v \omega_v \delta(\hat{\Sigma}_v - \hat{\Sigma})$$

and the sum is over all mechanically stable packings v .

Tests of the Stress-Based Ensemble

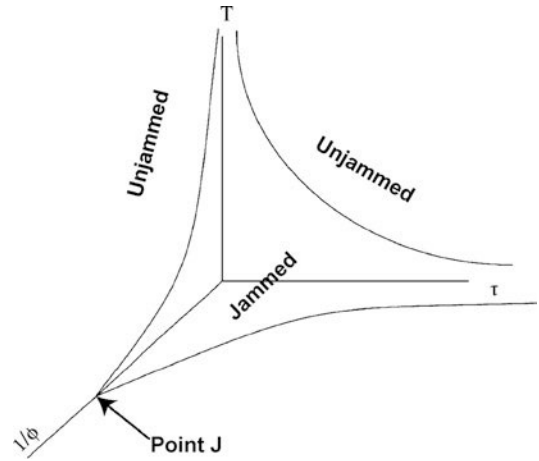
The ability to define an ensemble does not necessarily mean that real granular packings conform to this ensemble. The assumption of factorizability could break down or the frequency of occurrence of a packing, ω_v , could be history-dependent making the temperature or the ensemble concept not very useful. It is, therefore, essential to check the predictions of this ensemble against experiments and simulations.

This has been done for simulations of frictionless grain packings in two dimensions (Henkes et al. 2007) and it has been shown to work remarkably well. As a result of this comparison, an equation of state analogous to thermal equations of state, has been derived for frictionless grain packing approaching Point J (Henkes et al. 2007), that is consistent with the field theory constructed for Point J (Henkes and Chakraborty 2008).

Two applications of the stress-based ensemble to experiments probing the jamming transition will be discussed below.

Jamming Phase Diagram

About a decade ago, Liu and Nagel proposed that the jamming transitions in all systems, including the glass transition in supercooled liquids can be described by one unified framework through the jamming phase diagram and a special point in this phase diagram referred to as Point J (Liu and Nagel 1998). The proposed phase diagram,



Jamming of Granular Matter, Fig. 1 Jamming Phase Diagram proposed by Liu and Nagel. Adapted from (O'Hern et al. 2003)

shown in Fig. 1, delineates the boundaries of the jammed region in a phase space spanned by a temperature, density, and a load axis. The load axis captures the non-equilibrium aspects of these materials. For ideal spherical particles, the transition at Point J is a purely density-driven change, occurring at a critical packing fraction, ϕ_c between an amorphous solid state of dry granular packings and a state where the packings fall apart under any external stress (O'Hern et al. 2003). Recent experiments in granular packings have verified the existence of this, transition (Majmudar et al. 2007), as discussed in the section on experiments, and a theoretical description of this specific point is also emerging (Henkes and Chakraborty 2005; Wyart 2005; Wyart et al. 2005a).

In recent years, a theoretical framework has been developed (Kirkpatrick et al. 1989; Xia and Wolynes 2001; Bouchaud and Biroli 2004) that describes the complete phenomenology of the glass transition in supercooled liquids. There are similarities between this framework and the properties of Point J, but whether or not these diverse phenomena can be unified under the umbrella of universality is a subject of intense current research. The stress-based ensemble approach described earlier has been used to construct a coarse-grained field theory of Point J and the jamming transition (Henkes and Chakraborty

2005, 2008). Since field theories and scaling ideas based on them underlies universality in thermal phase transitions, the extension of this approach to granular materials hold out the promise of identifying different universality classes in the context of jamming.

The special properties of Point J are related to isostaticity (O'Hern et al. 2003). The discussion in section "Statistical Framework of Jamming" analyzes isostaticity for frictionless, spherical grains. In general, isostatic packings are those special ones where the number of contacts is just enough to provide mechanical stability (Tkachenko and Witten 1999). It has become increasingly evident (Donev et al. 2007) that isostaticity plays very different roles in spherical vs. non-spherical particles, which raises the question of whether Point J is special to frictionless spheres and disks. Also, it is not clear how generic the properties of this special point are, and whether or not it controls the behavior as one moves away from it in parameter space.

The jamming phase diagram of Liu and Nagel provides a framework for exploring the phenomenon of jamming in granular matter. Since temperature is not a relevant variable in the granular case, the phase space of interest would generically be the loading-density plane. The mechanical failure (or unjamming) of granular packings can occur because of (i) a vanishing bulk modulus (instability with respect to volume fluctuations) or (ii) a vanishing shear modulus (instability with respect to fluctuations of the shear stress). The state at Point J is an especially fragile one since both conditions (i) and (ii) are met. The stress state of the packing at this point is isotropic. In many instances, however, a granular material can be irreversibly deformed through the application of shear, and this process is also frequently referred to as unjamming. Specifically, for large enough shear stresses, a solid-like granular material will dilate, and fail in a process that typically leads to a locally weak and dilated region known as a shear band. This type of process has interesting analogues in the plastic failure of disordered glassy materials, in foams, in colloids and perhaps elsewhere. The tendency of densely packed granular materials to dilate under shear

was discovered by Reynolds (1885), and the adjustment of the density under shear is incorporated into critical state models of soil mechanics (Nedderman 1992). Although under shear, granular materials yield, and in some sense are 'unjammed', this process typically occurs under non-zero pressure as well as nonzero shear stress. Hence, 'unjamming' due to shear differs from the isotropic-stress state that occurs at Point J. In fact, the vast majority of experiments associated with jamming/unjamming are of this latter shear-induced process. There is compelling reason, discussed below, to think that plastic failure by shearing has a qualitatively different behavior than what occurs at Point J. For instance, jammed states also depend on whether they are isotropic or not, as shown by Majmudar and Behringer (2005a).

Given the dilatancy effects, and the differences between isotropically and anisotropically stressed states, we organize our discussion of jamming around a phase space spanned by the components of the Cauchy stress tensor (Eq. 3). This is a symmetric tensor, and in two dimensions we can, therefore, work with the isotropic pressure, P , and the shear stress τ . $P = \sigma_1 + \sigma_2$, and $\tau = \sigma_1 - \sigma_2$, where the σ_i are the principal stresses, i.e. eigenvalues of the stress tensor. Since the principal stresses are positive for granular materials, the physical space is enclosed by the $|\tau| = P$ and $P = 0$ lines. In fact, shear failure typically occurs for $|\tau| < P$. Point J lies at $P = 0$; $\tau = 0$. Along the $\tau = 0$ axis, simulations provide strong evidence of Point J having critical properties with, in particular, at least one diverging length scale (O'Hern et al. 2003).

If $\tau \neq 0$ then the jamming behavior could be quite different from that characteristic of Point J. Here, a useful analogy to equilibrium phase transitions may be the difference between a critical point, where a line of first-order phase transitions terminates, such as the ferromagnetic Curie Point which occurs at zero magnetic field and at a characteristic temperature T_c , or a tricritical point, which separates a region of second-order transitions from a region of first-order transitions. This type of a critical point arises in multicomponent, thermodynamic systems and a well-known

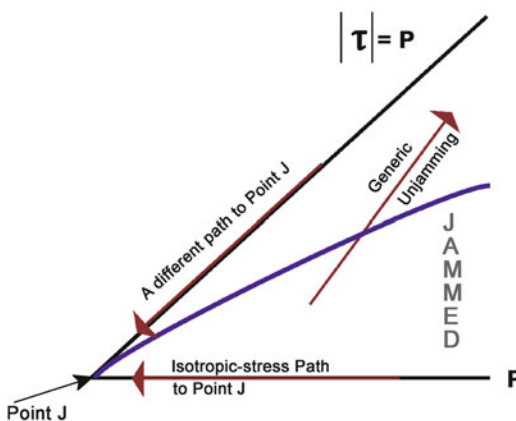
example is superfluidity in a mixture of He^3 and He^4 . For a high enough concentration of He^3 , the mixture undergoes a first order transition into two phases, and only one, the He^4 -rich phase is superfluid (Blume et al. 1971). A characteristic of a tricritical point is the existence of two diverging length scales, and in particular, there is a higher dimensional phase space that describes the various transitions. We present this discussion here purely as an illustrative example of a phase-transition scenario in which the signatures depend on what parameters are varied. We use the phase diagram of Fig. 2 to provide a framework for differentiating between the avenues available for approaching the jamming transition. In much of the literature, no distinction has been made, and we believe that has led to confusion. For each possible path, the transition can also be approached from the jammed side or the unjammed side. If $\tau = 0$, then the unjammed state is fluid-like in the sense that the system cannot respond elastically to any applied stress.

Below, we first provide an overview of the signatures of jamming observed as the transition is approached from the fluid-like side (section “Force Fluctuations, Dynamical Heterogeneities, Length and Time Scales in Granular Flows Approaching Jamming”), we then discuss the properties of jammed states under both shear and isotropic compression, as the jamming transition

is approached from the jammed side (section “Force Distributions, Length and Time Scales in Jammed States Near the Jamming Transition”). In section “Isostaticity and Point J”, we summarize the experimental and theoretical description of Point J and the associated length and time scales. Related areas of research that we do not include in this article at all, are the phenomenon of aging, non-equilibrium dynamics, and generalized elasticity for granular matter. We refer the interested reader to articles listed in the bibliography.

Force Fluctuations, Dynamical Heterogeneities, Length and Time Scales in Granular Flows Approaching Jamming

In this section, we review a number of physical and numerical experiments which give insight into the nature of the jamming process. Each approach has advantages and disadvantages. Numerics, typically consisting of direct simulations of the equations of motions for a set of particles, has the advantage that it is possible to easily explore parameter space. This approach is referred to as Molecular Dynamics (MD) or as Discrete Element Simulations (DEM), depending on the community. The disadvantage of simulation is that it is difficult to achieve an accurate representation of friction (often friction is neglected), and in addition, simulations are typically done only for spheres in 3D or disks in 2D (which we will refer to as isotropic particles). Experiments do not suffer from issues of accuracy of the interaction law, but it is very difficult to obtain quantitative data except at the boundary of 3D systems. Alternatively, it is possible to obtain information using quasi-2D systems, such as collections of disks, something that is also done frequently for simulations. Two-dimensional systems for both experiments and simulations can yield excellent quantitative information, but may leave open the question of generalizability to higher dimension. With these caveats, we turn to a review of both numerical and physical experiments that probe the jamming transition from the fluid-like side. Granular flows can be broadly divided into two categories, (a) inertial flows



Jamming of Granular Matter, Fig. 2 Jamming Phase Diagram in the space of components of the Cauchy stress tensor. The diagram shows a schematic in the $P - |\tau|$ plane, with arrows marking possible avenues of unjamming

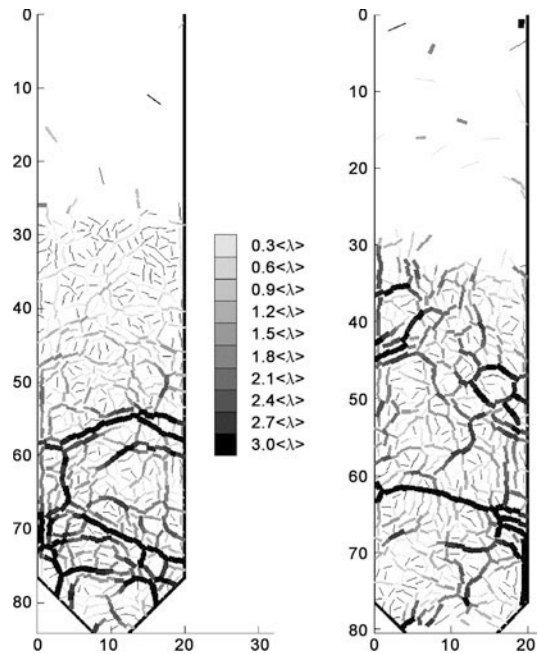
dominated by collisions between grains, and (b) quasistatic flows that involve extended contacts and slow evolution from one static, mechanically stable state to another.

Recent results from numerical simulations by Lois et al. (2007a, b) are of particular interest here. These authors studied shear flow of rigid particles which they modeled using contact dynamics, a version of MD/DEM for rigid particles. A particularly interesting discovery coming from these studies was the existence of a divergent correlation length for forces, associated with the formation of clusters, as the packing fraction approached ϕ_c from below. The presence of a divergent length scale reinforces the idea that jamming is actually a critical transition.

Evidence for critical properties also come from experiments on hopper flow by Longhi et al. (2002). These experiments involved a quasi-2D flow of monodisperse spheres out of a hopper-shaped container. Necessarily, the presence of flow implies that the states studied here were unjammed. As the particles moved by, a small high speed force gauge mounted near the outlet of the hopper yielded the impulse of individual collisions. The collisions could be clearly identified because of a large separation of scales between the duration of contact, and time between contacts. The distributions of these impulses, at large impulses were roughly exponentially distributed, and independent of the flow rate. At small impulses, the distributions evolve with flow rate with a relative increase of small impulse events as the flow rate decreases. A more interesting statistic is the distribution of τ 's, the time between successive collisions. As the jamming transition was approached, these distributions approached a powerlaw, $P(\tau) \propto \tau^{-3/2}$.

An MD simulation of hard disks, in a geometry designed to mimic the experiments of Longhi et al. (2002), provided an explanation for the evolution of the impulse distribution in terms of increasing velocity correlations (Ferguson and Chakraborty 2006; Ferguson et al. 2004). These correlations also led to a qualitative explanation of the changes in $P(\tau)$ (Ferguson and Chakraborty 2006), which occur because the average time between collisions *decreases* as the flow velocity

decreases while at the same time the time taken for a particle to fall through its own diameter increases. This leads to a large separation of time scales and a range of times over which the dynamics is scale invariant. The simulations provided strong indications that these physical effects owe their origin to the existence of chains of frequently-colliding particles. In addition, it was shown that these collision chains could be interpreted as stress chains with the stress measured through momentum transfer [20, the counterpart of force chains in this system of flowing hard particles. Figure 3 is a snapshot of a simulation illustrating the stress chains for two different flow rates, as controlled by the width of the opening at the bottom of the hopper. More recent work on this system of hard disks has provided evidence for the existence of dynamical heterogeneities identified through the displacements of grains (Ferguson and Chakraborty 2006).



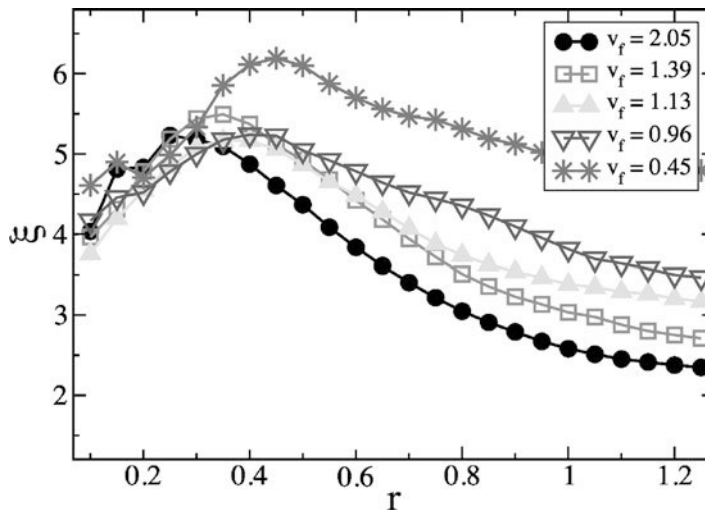
Jamming of Granular Matter, Fig. 3 Stress chains. The grayscale plot is constructed by scaling the collisional stress by the average collisional stress ($\langle \lambda \rangle$) obtained by coarse graining over many collisions. Close to jamming, the coarse-graining time is much shorter than the time taken by a particle to fall through its own diameter (Ferguson and Chakraborty 2006)

A length scale can be extracted from measurements of spatio-temporal correlations of these heterogeneities. As in supercooled liquids, there is a length scale that has a peak at a characteristic time. Both length and time scales depend on the average flow velocity, growing as the system approaches jamming. The increase in length, however, is not as dramatic as in supercooled liquids or in experiments on air-driven granular beads (Keys et al. 2007). As an example of the characteristic shapes of the length versus time curves observed in all of these systems, supercooled liquids, inertial and quasistatic granular flows, we show a set of data from the MD simulations of hopper flow in Fig. 4 (Ferguson and Chakraborty 2007).

Pouliquen et al. have carried out a series of experiments on flow down chutes/inclined planes (Pouliquen 2004; Pouliquen 1999). These studies have shown that there is a range of inclination angles, θ , for the chute for which it is possible to obtain steady state flow, and that the depth of the flowing layer, h , depends on θ . The flow stops if h is smaller than an inclination-angle-dependent function, $h_{\text{stop}}(\theta)$. Data for the depth-averaged

velocity, u can then be expressed in terms of a flow rule, $u/(gh)^{1/2} = \beta h/h_{\text{stop}}(\theta)$, where β is a material-dependent $O(1)$ constant. Following a suggestion by Ertas and Halsey (2002), Pouliquen (2004) explored the possibility that there might be observable spatial correlations for the surface velocity which would signal the onset of jamming. Indeed, such correlations exist, and they grow as the inclination angle of the chute is lowered, i.e. as the system approaches the jammed state.

Kolb et al. (2004) have studied the response of a jammed 2D layer to a localized cyclic displacement. This process was carried out quasistatically, and in such a way as to locally unjam the system. More specifically, the experiment consisted of a bidisperse layer of disks, inclined from the vertical, so that the system was normally jammed. An intruder particle having a diameter corresponding to the larger of the two grain sizes, was displaced periodically in time by small amounts. These local displacements led to a much longer range set of displacements, part of which was reversible, but part of which was irreversible. This long-range response is suggestive of a critical-like response for states near jamming.



Jamming of Granular Matter, Fig. 4 Lengths scale, ξ , associated with the heterogeneity of dynamics as a function of the mean square displacement, r , of particles in MD simulations of a two-dimensional hopper flow (Ferguson and Chakraborty 2007). This length scale, extracted by analyzing the spatial correlation between displacements of particles (Hurley and Harrowell 1995; Perera and

Harrowell 1996), peaks at a characteristic displacement which can be related to a characteristic time at which the dynamics is most heterogeneous. This plot is qualitatively similar to ξ vs. time plots observed in the experiments of Durian et al. on air-driven beads, in the experiments of Dauchot et al. on particles driven by oscillating shear (see text), and in supercooled liquids

Drocco et al. (2005) have used MD to simulate the behavior of a 2D particle that is pushed through originally static bidisperse packings of similar particles. The packings reside in a square geometry with periodic boundary conditions, and are prepared at packing fractions below the jamming value for this system. The authors first focus on the intruder velocity, which becomes increasingly intermittent as $\phi \rightarrow \phi_c$ from below. To characterize the intermittency, Drocco et al. use multifractal analysis to compute moments, $M(q) = \int dv P(v) v^{-q} \propto (\phi_c - \phi)^{\tau(q)}$, and present evidence for multiscaling. Of particular relevance here is a demonstration that as $\phi \rightarrow \phi_c$, the number of disks, n , that move in response to a fixed pushing distance for the intruder grows rapidly. These authors use data for the number of moving disks vs. ϕ to estimate a correlation length, which diverges as $\xi \propto (\phi_c \phi)^{-\nu}$, with $\nu = 0.71 \pm 0.12$. These numerical studies have an interesting parallel with experimental studies by Geng and Behringer (2005) which yielded the force needed to push a disk through a channel of other disks in the jammed state. These data yielded a pushing force that also became increasingly intermittent on approach to ϕ_c , in this case from above, and a mean force that vanished as $(\phi - \phi_c)^\alpha$ with $\alpha = 1.5$.

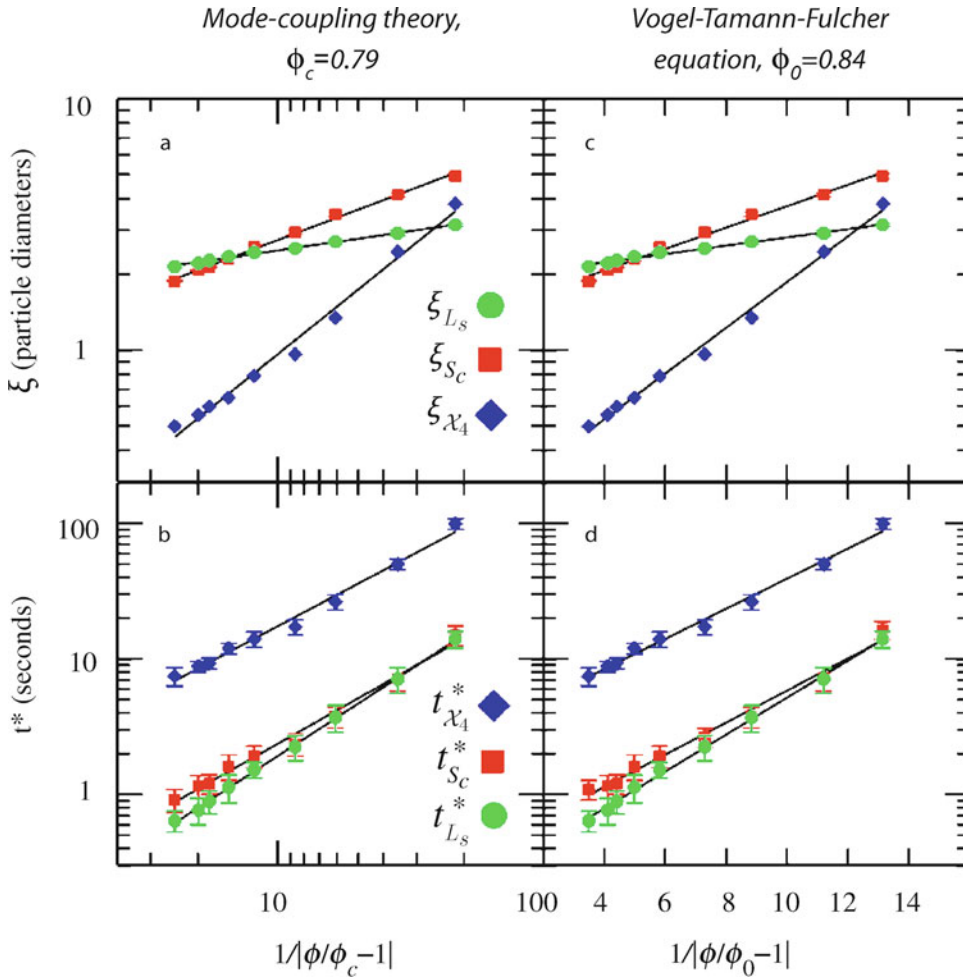
Dauchot et al. (2005) have studied correlations in systems of particles in 2D that are subject to small-amplitude oscillating shear. In this case, simple shear was applied, meaning that a rectangular sample was alternately tilted into a parallelogram to the right, then left. Dauchot et al. were particularly interested in characterizing the spatio-temporal fluctuations of systems near jamming. An image was obtained each time that the system was returned to the rectangular state, and the location of each particle was then determined. From these data, the authors first calculated a measure of individual particle motion, the self-intermediate scattering function, $F_s = \langle \hat{F}_s(k, t) \rangle = N^{-1} \sum_j \langle \exp[-ik(r_j(t) - r_j(0))] \rangle$. The results for $F_s(k, t) \propto \exp[-(t/\tau(k))^{\beta(k)}]$ indicate Brownian diffusion at small k , but a different behavior at large k , i.e. smaller spatial scales, where β is smaller than unity: a stretched exponential. They attribute this behavior to

dynamical heterogeneities, and they further quantify the nature of these dynamical heterogeneities by analyzing length and time scales associated with fluctuations of $\hat{F}_s(k, t)$, as has been done for supercooled liquids. The analysis identifies a moderate length scale associated with the fluctuations, in agreement with the type of length scales that have been observed in supercooled liquids.

Durian et al. (Keys et al. 2007) have studied dynamical heterogeneities in a system of air-driven granular beads as a function of the packing density. Using multiple measures of lengths associated with dynamical heterogeneities, these authors demonstrate that there are length and time scales, which grow with the approach to Point J. They also show that the increase in these scales follows the Vogel–Fulcher–Tamann form: a form that is associated with supercooled liquids approaching the glass transition (Ediger et al. 1996). Figure 5 shows length and time scales extracted from different measures of dynamical heterogeneities as a function of the packing fraction. The fits are to the predictions of Mode-Coupling-Theory of the glass transitions and to the Vogel–Fulcher–Tamann form, which implies an exponential divergence at a packing fraction ϕ_0 . Interestingly, the value of ϕ_0 is very close to the ϕ_c associated with Point J (Keys et al. 2007).

Force Distributions, Length and Time Scales in Jammed States Near the Jamming Transition

An interesting premise is that the distribution of interparticle contact forces, $P(F)$, can provide insight into the nature of the global granular state of a system. In particular, it may be useful as a tool to distinguish jammed from unjammed or nearly unjammed states. It is also an important indicator of the overall stress state of the system, as demonstrated in experiments (Majmudar and Behringer 2005a, b) and theory (Snoeijer et al. 2004d, e). Since the transition to a deforming state in a dense granular material has often been obtained by shearing, there have been a number of studies that have addressed this case (Miller et al.



Jamming of Granular Matter, Fig. 5 Data for length (ξ) and time (t^*) showing an increase in these scales associated with dynamical heterogeneities in a system of air-driven beads. Reprinted from (Keys et al. 2007)

1996; Howell and Behringer 1999; Veje et al. 1999; Daniels and Behringer 2005a, b, 2006; Hartley and Behringer 2003; Corwin et al. 2005a). In particular, Howell et al. (Howell and Behringer 1999; Veje et al. 1999) have directly probed the transition that occurs when the density of a sheared granular sample is reduced to the point where stresses vanish. Other studies have probed the nature of steady granular shear (Miller et al. 1996; Daniels and Behringer 2005a, 2006; Hartley and Behringer 2003; Corwin et al. 2005a).

We discuss below several recent experimental studies which help elucidate this point. Here, we focus first on sheared, and then on isotropically confined systems.

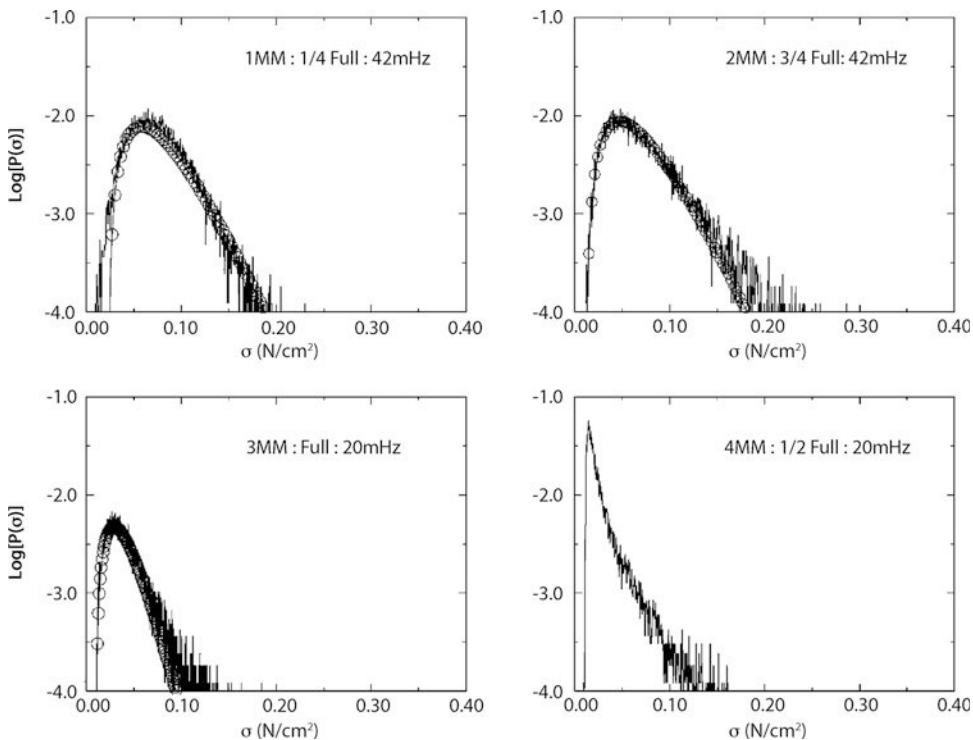
Sheared States

Fluctuations, their distributions and their correlations, are interesting for a number of reasons. First, they can reveal the nature of short and long range behavior. In addition, they provide a useful test of model behavior, and they help to identify key parameters. One of the earliest experimental characterization of force fluctuations in dense granular materials was by Miller et al. (1996). These experiments involved the shearing of an annular layer of glass spheres. A rough plate sheared the top of the annular layer and the pressure was measured at the bottom of the layer using a force gauge of fixed area. These studies are typical of many quasi-static shearing experiments.

The system remains close to a static state, so that if the shear stress is reduced, the system typically reverts to a static state with only small changes in the particle configurations. However, enough shear is applied during steady-state motion that the system unjams intermittently, presumably associated with a short-term weakening of the shear modulus. In some sense, this type of motion straddles the jammed-unjammed boundary, first on one side, and then on the other. In addition, it is typical that a region of the material weakens and forms what is called a shear band. Because a shear band has lower shear strength than other regions, it tends to persist as a localized region where most of the shear deformation occurs. This process is typified by local structural rearrangements and frequently with large force fluctuations. The fluctuations in the experiments of Miller et al. showed a kind of rate-independence. They also yielded information on the force and pressure

distributions, Fig. 6. The force detector was of fixed diameter, so by varying the particle diameter, it was possible to tune the number of particles contacting the detector from a small number, to ~ 100 particles. For the largest particles, this provided, at least roughly, information on $P(F)$. For the smallest particles, one might expect that the force fluctuations would be substantially averaged out, yielding something more like the mean pressure. We show data for the PDF's of the measured forces/stresses, in Fig. 6. If the forces acting on the detector from individual particles were uncorrelated, then one would expect that this would narrow as $N^{1/2}$, i.e. as the square root of the number of contacting particles, and evolve towards a gaussian. In fact, there is much less narrowing than would occur for uncorrelated forces from individual particles.

Two recent studies of 3D continuously sheared systems provide additional insight (Daniels and

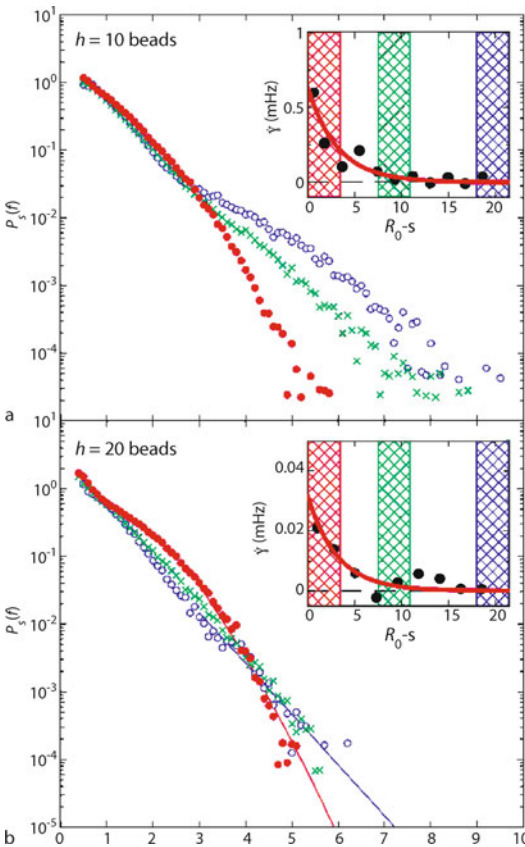


Jamming of Granular Matter, Fig. 6 Distributions of forces measured at the base of a continuously sheared layer of glass spheres, for different sphere diameters of 1 mm, 2 mm, 3 mm and 4 mm, as indicated, and a fixed detector

diameter of 1.0 cm. The other numbers give the depth of the granular layer as a fraction of the full height, 4.1 cm, and the shearing rate (Miller et al. 1996)

Behringer 2005a, b, 2006; Corwin et al. 2005a). Both systems yield PDF's of forces at the boundaries, and it is interesting to contrast the two sets of results.

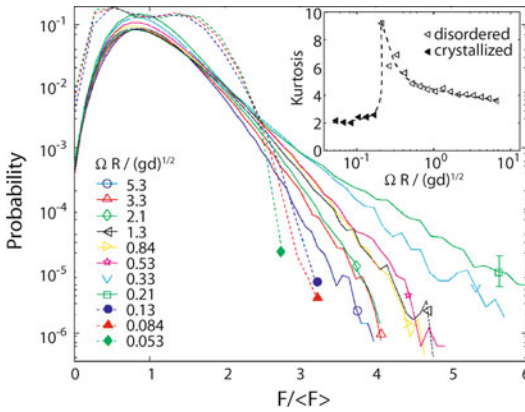
Corwin et al. (2005b) have recently presented extensive experiments using a photoelastic technique to measure forces at the bottom boundary of a cylindrical container filled with spherical particles and sheared from above. In the steady state, particles in the bottom layer located beyond a characteristic radius, R_b , exhibited dynamic shear flow, specifically, a shear band. Particles located closer to the center than this radius remained in a permanently jammed state and moved as a solid body. Corwin et al. obtained $P(F)$'s, with a particular focus on the region above R_b . These distributions, Fig. 7, show an enhancement for small F , and qualitatively resemble those



Jamming of Granular Matter, Fig. 7 $P(F)$ in sheared and non-sheared zones. Reprinted from (Corwin et al. 2005b)

obtained by Howell et al. for 2D shear flow, as discussed below. Corwin et al. proposed that these distributions can be related to an effective temperature, T_{eff} , by noting that the distribution of forces and the radial correlation function, assuming forces described by a potential, $V(r)$, should satisfy $P(F)dF = G(r)dr$, where $G(r)dr$ is the radial distribution function. They then drew on the small- r thermal result $G(r) \propto r^{-2} \exp[-V(r)\beta]$ where $\beta = 1/(k_B T)$ (in this case, T should be replaced by T_{eff}). This argument leads to the prediction that at low forces, one should expect $P(F) \propto F^{-1/3}$, a prediction that describes their data well. The resulting effective temperatures obtained from this analysis are insensitive to shear rate and also to the height of the granular layer.

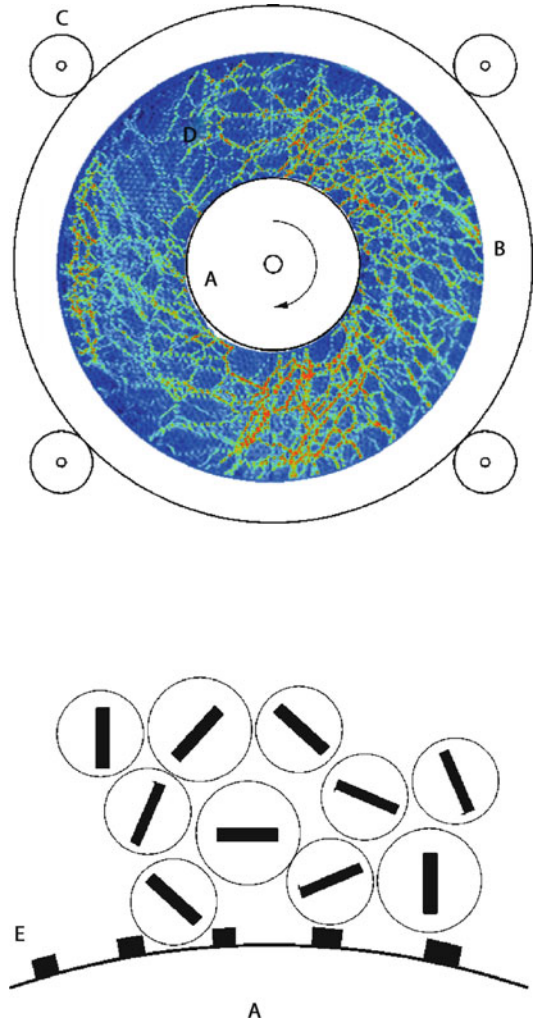
Other recent studies of sheared 3D particles, this time in an annular channel, were carried out by Daniels and Behringer (2005a, b, 2006). In these experiments, the overall geometry was similar to Miller et al. (1996) but in addition, the bottom boundary of the experiment was shaken with peak accelerations that typically exceeded the acceleration of gravity. The shaking motion allowed the system to find not only a jammed state, but actually a crystalline state. At high enough shear, the crystal melted, producing a shear-banded, disordered, and flowing state. This transition was clearly evident in $P(F)$. Here, F is the force exerted by particles on a transducer that is roughly three particle diameters across. In the crystalline state, $P(F)$, Fig. 8, had an overall envelope that was roughly gaussian, but that had two peaks which were induced by the vibrational motion. In the melted, disordered state, $P(F)$ resembled the distributions of Miller et al. As the transition to the ordered state was approached from the disordered state, the tail of $P(F)$ became increasingly extended. Associated with this long tail were increasingly large volume fluctuations. In fact, the variance of volume fluctuations and the various moments, including the kurtosis of the $P(F)$, showed a cusp at the transition. This is particularly interesting in the present discussion, since the volume variance should be proportional to the derivative of the Edwards entropy (discussed in section “Statistical Framework of



Jamming of Granular Matter, Fig. 8 Distributions for the pressure/force at the bottom of an annular layer of spheres that is sheared at a rate Ω , from above, and that is vibrated from below with a peak acceleration of $\Gamma = 2.0$, in units of g . R is the mean radius of the annulus, and d is the particle diameter. The two-peaked distributions are in the crystalline phase, and the single-peaked distributions are in the disordered phase. The inset shows the Kurtosis of the distributions as a function of a scaled shear rate. The cusp in the kurtosis is caused by the stretching out of the distributions as Ω is decreased from a large value where the state is disordered

Jamming”) with respect to compactivity, i.e. the Edwards ensemble analogue of a specific heat.

A relatively early demonstration of jamming properties was the work of Howell et al. (Howell and Behringer 1999; Veje et al. 1999) These experiments consisted of photoelastic disks which were sheared in an annular Couette geometry, as in the sketch of Fig. 9. The boundaries of the apparatus consisted of a fixed outer ring, and in inner wheel whose rotations provided the shear. The particles were confined in the horizontal directions by the ring and wheel, and they rested on a smooth powder-lubricated horizontal Plexiglas sheet. Data were obtained in a steady state after the system had been sheared for roughly 30 min. The low shearing rate meant that that the process was quasi-static and hence always close to equilibrium. In particular, if the shearing was stopped, the majority of the force chains remained unchanged following an initial relaxation. Over long times, more of the force chains decayed, but that process was logarithmically slow (Hartley and Behringer 2003). In these experiments, the average force per particle (roughly a measure of



Jamming of Granular Matter, Fig. 9 Sketch of the basic two-dimensional Couette shear apparatus, with an overlaid image showing the heterogeneous force structure that occurs. Photoelastic particles are confined within an annular region whose boundaries are a rotating inner wheel, and a fixed outer ring. Also shown is a blow-up sketch indicating the rough nature of the shearing wheel, and the fact that the photoelastic disks are marked with small bars for tracking purposes. In the false-color image from this experiment, red corresponds to particles experiencing a large force, and blue 0 to particles experiencing a small force (Howell and Behringer 1999; Veje et al. 1999)

the particle-scale pressure) was obtained by calibrating an applied compression to the photoelastic response of the particles. These experiments, as well as those of Daniels and Behringer (2005c, 2006), showed an increase of the mean stress with

the shear rate that varied linearly as the logarithm of the shear rate. The logarithmic strengthening has been shown to be consistent with predictions of the stress-based ensemble, described in section “Statistical Framework of Jamming” (Behringer et al. 2008).

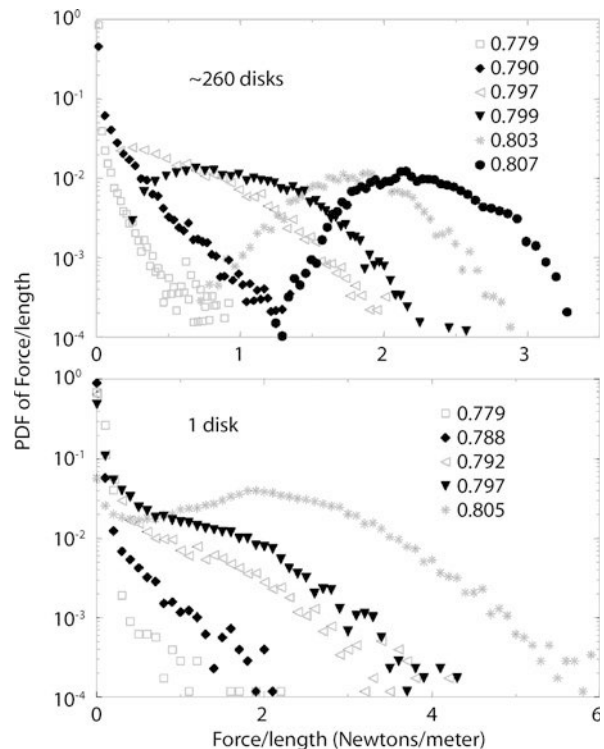
Several observations concerning these experiments are noteworthy. First, these experiments yielded the force distributions for the mean force on a particle, and also for averages over multiple particles. Second, they showed a kind of critical slowing down as the packing fraction, ϕ , approached the jamming transition from above, and third, they showed that a characteristic length scale associated with the mean length of force chains grew as $\phi \rightarrow \phi_c$ from above. We reproduce these results in Figs. 10 and 11 (Howell and Behringer 1999).

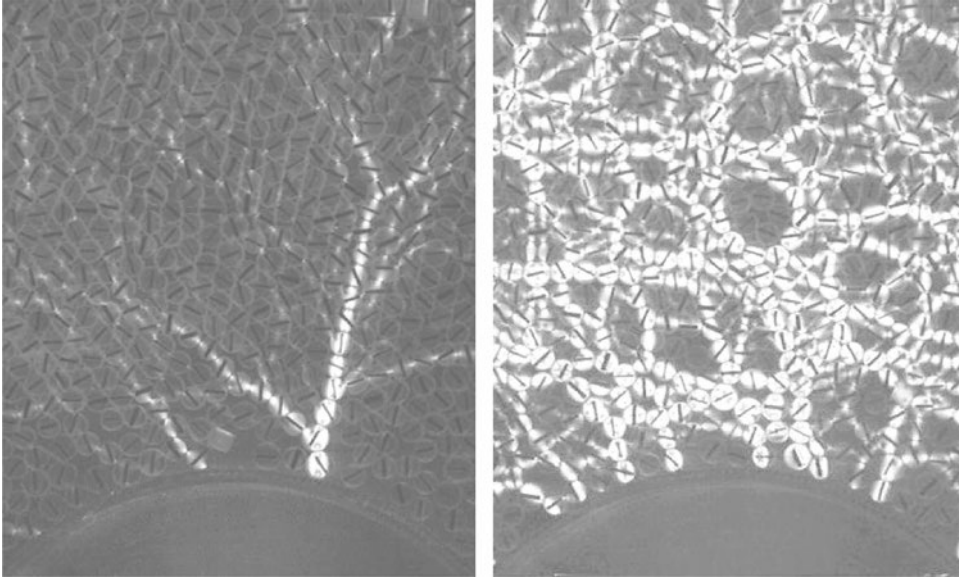
The distributions for the single particle forces depend on the distance to ϕ_c . For ϕ close to ϕ_c , the distributions fall off roughly exponentially with large force, although there is an extra density of low force states. These distributions are nominally rather similar to single particle force

distributions which were observed for particles at the boundaries of the 3D sheared system by Corwin et al. (2005a). For larger ϕ , the distributions from the 2D shear experiments developed a peak which gradually migrated to larger force as the density grew. The distributions for the force on collections of particles also depend on the density. Close to jamming, they are similar to the single-particle distributions; at larger density, they evolve to a more gaussian shape. The multi-particle-force distributions are then interesting on several accounts. First, they provide a way to compare to earlier 3D pressure measurements (i.e. force measurements involving multiple particles) and they also give some sense of force correlations. That is, if the force on a given particle were uncorrelated with the force on other nearby particles, then the distribution for the forces experienced by a collection of particles would typically evolve to a gaussian as the number of particles in the collection increases. This is consistent with what is observed for larger ϕ , but not with what is observed for ϕ near ϕ_c . Hence, by inference, there exist correlations for the particle-

Jamming of Granular Matter, Fig. 10

PDF's from the 2D Couette experiment for single particles (bottom) and for collections of particles lying within an extended region. Numbers indicate the packing fraction. This system has a critical value of $\phi = 0.776$ where stresses vanish. Note that the distributions of forces for single particles develops a maximum for large packing fractions. The distributions for forces for collections of roughly 260 particles in a contiguous region show a much stronger peak as ϕ increases, and no peak when ϕ is just above ϕ_c . This suggests that correlations in force grow as $\phi \rightarrow \phi_c$ (Howell and Behringer 1999)





Jamming of Granular Matter, Fig. 11 Photoelastic images from the Couette shear experiment at a low (left, $\phi - \phi_c = 0.001$) and high (right, $\phi - \phi_c = 0.031$) distance

scale forces for near-critical ϕ 's. To make this idea somewhat more precise, we show in Fig. 13 what happens to the PDF for the collective force for groups of particles acting on a detector if a) the forces exerted by each particle are chosen from q-model like distribution (Coppersmith et al. 1996), and b) the forces exerted by any one particle are uncorrelated with any of the others. Specifically, the distribution narrows as $N^{-1/2}$.

The results from the 2D Couette shear for the velocity profiles vs. ϕ and also data for the characteristic force chain length both suggest that the system becomes increasingly inhomogeneous, in terms of force transmission as $\phi \rightarrow \phi_c$ from above. In particular, the typical force chain length clearly grows, although it does not necessarily diverge, in these experiments on approach to ϕ_c . In fact, given our discussion above concerning a $P - \tau$ phase diagram, we might well expect that in shear experiments one approaches point J along a path which lies above the P axis. Figure 11 contrasts a photoelastic image from Howell et al. (Howell and Behringer 1999) taken well above ϕ_c with an image for ϕ just slightly above ϕ_c . In the higher ϕ case, the force network is more nearly homogeneous, in contrast to the case just

from the unjamming point of this system. Note the long filamentary chains near ϕ_c and the tangled network far from ϕ_c (Howell and Behringer 1999; Veje et al. 1999)

above ϕ_c . For the latter case, only a handful of particles are visibly in a force chain. (Here, some caution must be taken, since there is a force below which the photoelastic image is too weak to be resolved.) Nevertheless, only intermittently is there a strong enough contact at the shearing wheel so that a particle is entrained by the shearing wheel. This leads to critical slowing down which is evident in the mean velocity profiles, Fig. 12.

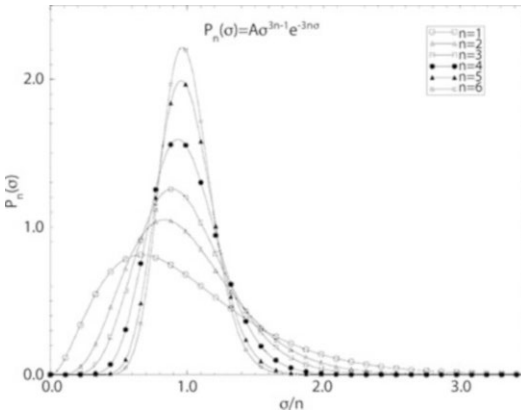
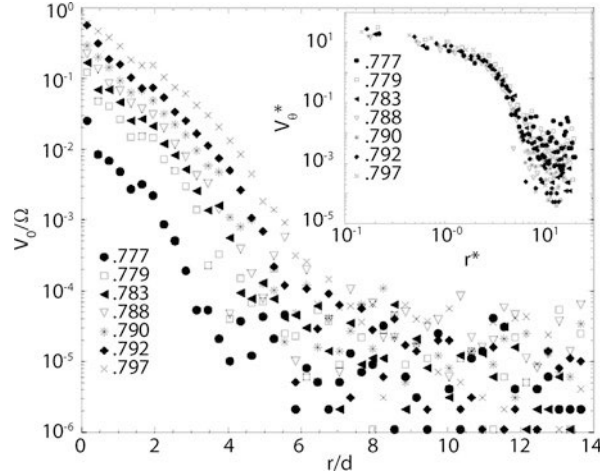
Isotropic vs. Anisotropic Stress States

As discussed above, the nature of jamming depends, in what appears to be a significant way, on the presense or absence of shear stresses. The experiments and simulation discussed above have all involved sheared states. Here, we consider simulations and experiments which are for isotropic systems, and which focus on an approach to jamming that involves the dense/jammed side (Fig. 13).

Numerical Simulations The phenomenon of jamming in isotropically stressed states has been extensively investigated through numerical simulations of frictionless, spherical grains in both two and three dimensions (O'Hern et al.

Jamming of Granular Matter, Fig. 12

Data for the mean azimuthal velocity profiles vs. radial distance from the shearing wheel for the 2D Couette experiment. These data are normalized by the angular speed, Ω , of the shearing wheel. Inset shows that these data collapse onto a single curve when scaled a function $\propto(\phi - \phi_c)^1$ (Howell and Behringer 1999)



Jamming of Granular Matter, Fig. 13 Computed PDF of the force per particle exerted by collections of n particles whose forces are uncorrelated and are drawn from exponential distributions. The absence of correlations leads to the expected narrowing by $n^{-1/2}$

where N grains each with volume V_p were packed in a box of volume V . For polydispersed assemblies of grains, the definition of the packing fraction can be easily generalized. An interesting protocol that was developed in trying to identify Point J was that of inflation or deflation, in which the pressure of a quenched state was measured, and the radius of the grains were scaled up or down by small factors until the pressure was zero (within a numerical tolerance). For each initial configuration (v) the zero pressure state corresponded to a particular packing fraction, ϕ_v^c . At this packing fraction, the grains just touched and if the packing fraction was reduced below this, no mechanically stable states could be obtained. The crucial findings of these simulations are summarized below:

2003; Makse et al. 2000). This work includes in particular, a series of MD simulations by O'Hern et al. (2001, 2002, 2003). This series of simulations led to the introduction of the existence of a critical point at zero shear and a critical density, ϕ_c : Point J. The simulations probed the nature of the packings of spherical grains (disks in two dimensions), which interact via a short-range, soft-repulsive potential, meaning that there are no long-range interactions, and that there are purely repulsive normal forces which come into play when the grains are compressed. The packings were obtained by quenching from initial random states with a packing fraction $\phi = NV_p/V$,

1. If properties such as pressure, shear modulus, and average number of contacts of the packings are measured as a function of $\phi_v - \phi_v^c$, then the properties are found to be independent of v .
2. The pressure, bulk modulus and shear modulus all go to zero as some power of $\phi_v - \phi_v^c$. The exponent of the power law for the pressure and the bulk modulus follows from the force law but the shear modulus has a non-trivial exponent that indicates non-affine displacements (O'Hern et al. 2003; Ellenbroek 2007).
3. The distribution of ϕ_v^c becomes narrower with increasing system size and the mean

- approaches the Random Close Packing value (Donev et al. 2004).
4. Above ϕ_c , the average number of contact follows a power law: $\langle z \rangle - z_{\text{iso}} \propto (\phi - \phi_c)^{1/2}$.
 5. The vibrational density of states exhibits increasing weight at low frequencies as Point J is approached, and the lowest frequency below which the packing behaves as a normal elastic material approaches zero (Wyart et al. 2005b).
 6. Two different diverging lengths scales can be identified from analysis of the vibrational spectrum. These two length scales diverge with *different* exponents (Silbert et al. 2005), and therefore indicate the existence of multiple diverging correlation lengths at Point J.
 7. The force distribution, $P(F)$ is sensitive to the distance from ϕ_c , and approaches an exponential as the packing fraction approaches ϕ_c .

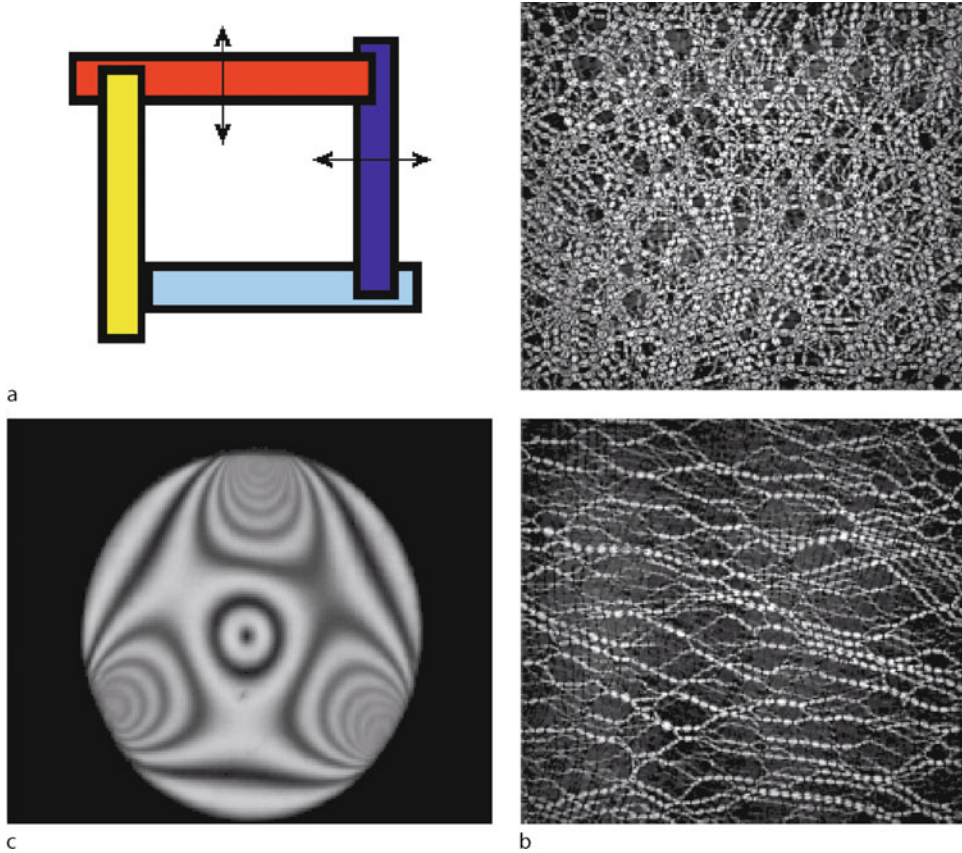
Experiments Regarding physical experiments for the isotropic case, we are aware of only one set of results, namely data by Majmudar and Behringer (2005a). These results depend crucially on using photoelastic techniques in a much more precise way to obtain contact forces (Majmudar and Behringer 2005a, b). Hence, we discuss briefly how this approach works. The basic idea is the following. For given contact forces acting on a disk, the stress field within the disk is determined. The stress field in turn determines the photoelastic response. Specifically, for a ray that traverses a slab of photoelastic material of thickness L that is sandwiched between crossed circular polarizers, the transmitted intensity is $I = I_0 \sin^2[(\sigma_2 - \sigma_1)CL/\lambda]$. Here, σ_2 and σ_1 are the principal stresses in the plane of the slab (or disk), C , the stress optic coefficient is a property of the material, and λ is the wavelength of the light with intensity I_0 . Thus, contact forces determine stresses which in turn determine the photoelastic pattern. The idea is to carry out the inverse of this process. Specifically, from the photoelastic pattern, determine the applied forces. This can be done efficiently in the case of a disk because there is a closed form relation for the stress field generated by any number of contact forces.

MB have developed such an inverse process and applied it to systems of photoelastic disks that have been prepared in well defined stress/deformation states. The particularly important aspect of these experiments is that they have yielded the only experimental data, to our knowledge, for contact forces inside a granular sample, although a number of other experiments have yielded forces at boundaries. This point is important; theoretical studies by Snoeijer et al. (2004d, 2004e) indicate that force distributions for contacts at boundaries and in the interior of a sample differ substantially.

Figure 14 shows a rough schematic of a biaxial tester (or biax) and resulting photoelastic response images for different types of applied stresses (Majmudar and Behringer 2005a). The purpose of the biax is to prepare states of well controlled strain or stress. The biax is constructed so that the space between opposing pairs of walls can be set to any convenient value. The particles in this sample are bidisperse disks, with about 80% having a smaller diameter (0.8 cm) and 20% having a larger diameter (0.9 cm). Bidisperse packings of this sort typically have no long-range crystalline order, although they tend to show hexagonal bond order.

Manifestly, the force chain structures that result from pure shear vs. isotropic compression, Fig. 14b, are substantially different. Pure shear induces force chains that extend nearly straight and uninterrupted over the compressional direction of the biax. This is intuitively reasonable, since the pure shear state is achieved by compressing, hence strengthening contacts in one direction, while dilating the sample, thus weakening contacts, in the perpendicular direction. By contrast, for an isotropically compressed sample, the force network consists of a dense tangle of short force chain segments.

Various statistical measures reflect the fact that shear and isotropic compression yield qualitatively different states. We consider first, the distributions of contact forces, $P(F)$, which are given in Fig. 15. For convenience, forces are normalized by $\langle F_n \rangle$, the mean normal force. The figures show separate distributions for the normal and tangential contact forces. Although the distributions for



Jamming of Granular Matter, Fig. 14 Biaxial experiment. (a) Sketch illustrating the fact that two walls of the experiment are moveable, allowing the creation of arbitrary (rectangular) deformations and stress states. (b) Two different stress states produced by top: isotropic

compression, and bottom: pure shear, i.e. compression in one direction and equal dilation in the opposite. (c) A closeup image of a single photoelastic particle showing the detailed photoelastic pattern that is used to deduce contact forces (Majmudar and Behringer 2005a)

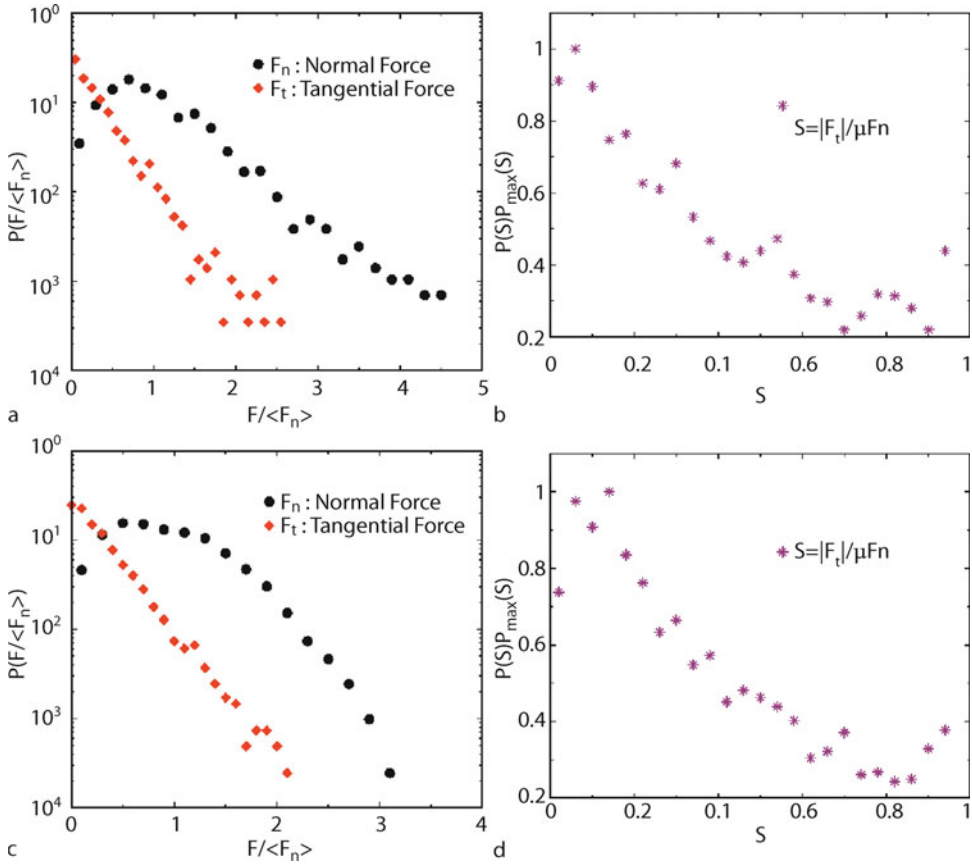
the tangential forces are always exponentially distributed, regardless of the stress state, the same is not true for the normal force distribution. These clearly reflect the stress state, with a state of pure shear showing a roughly exponential fall-off at large F , and with a state of isotropic compression showing a much more rapid fall-off with F . In fact, these distributions are consistent with recent entropy-based arguments by Snoeijer et al. (2004d) and by Tighe et al. (2005b). In both cases, the distributions for the normal forces show a peak at a force comparable to the mean. Perhaps a better measure of the difference between the shear and isotropic deformations is given by the force correlation function, which is significantly longer range along the force chain

direction of the sheared case, than any direction for the isotropic case (Majmudar and Behringer 2005a). We show these results in Fig. 16.

Isostaticity and Point J

Isostaticity and Random Close Packing

This section is devoted to a geometrical picture which offers a perspective that is complementary to the statistical ensemble picture. The geometrical approach is focused on mathematically precise descriptions of packing of infinitely rigid particles (Donev et al. 2004, 2007). In this statistical geometric picture, packings are characterized by the type of jamming: local, collective or strict. In the

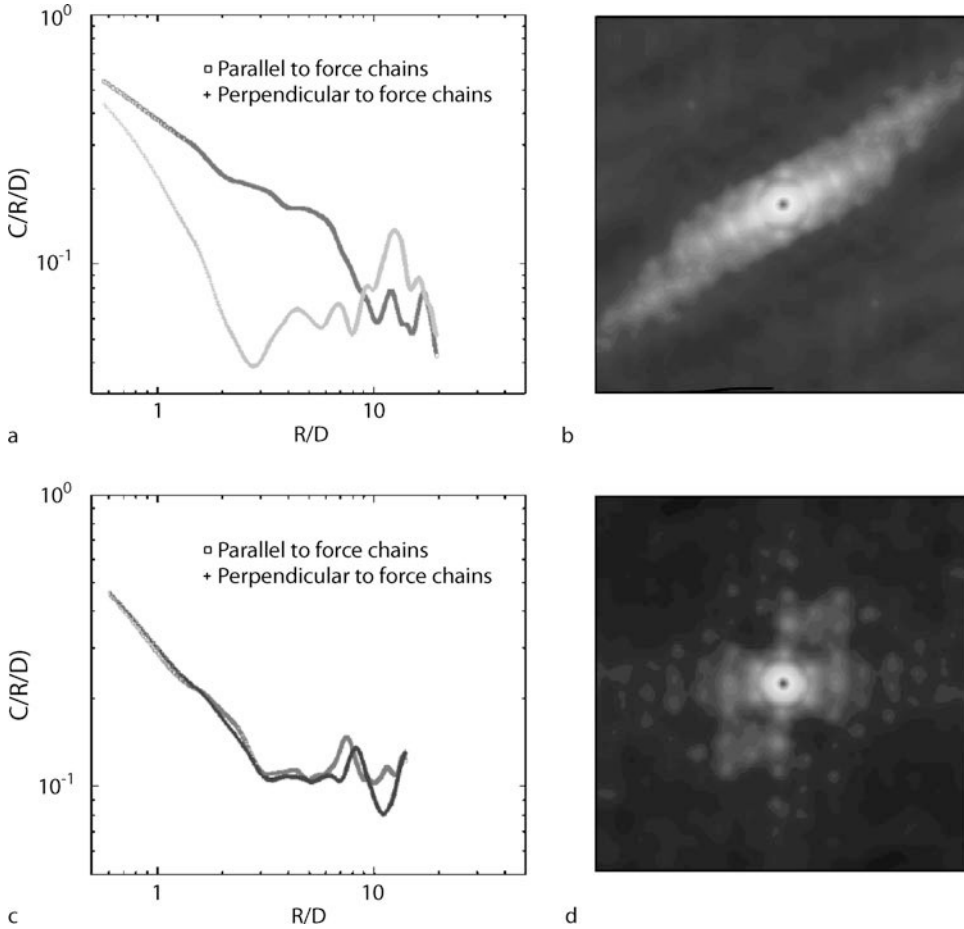


Jamming of Granular Matter, Fig. 15 Distributions of forces for pure shear (top) and isotropic compression (bottom). Parts (a and c) give distributions of normal (F_n) and tangential (F_t , frictional) forces, all normalised by the

appropriate mean normal force, $\langle F_n \rangle$. Parts (b and d) indicate the mobilization of friction, where the variable S indicates fully mobilized (at the point of slipping) friction when $S = 1$ (Majmudar and Behringer 2005a)

hierarchy of jammed states, locally jammed states are ones where each particle in the system is locally trapped by its neighbors. Collectively jammed states are ones where all finite subsets of particles are trapped by their neighbors, and strictly jammed states are collectively jammed configurations for which no global, volume-nonincreasing deformations are possible (Donev et al. 2004). In addition, the degree of order in the packings is characterized by an order parameter or an order metric (Torquato et al. 2000). The emphasis in this approach is to understand the existence of packings, not their statistical weight in any dynamical protocol. The geometrical approach applies to infinitely rigid bodies which is an idealization of real particles, but the classification into jamming categories and a precise

understanding of the nature of packings which can exist as the packing fraction is varied provides a framework onto which the statistical description can be superposed. There are a few special points on a phase diagram in the order-packing fraction space: (a) the maximally random jammed state (MRJ) is an extremal point corresponding to the least ordered, strictly jammed state, (b) the random-loose-packed (RLP) state is another extremal point corresponding to the lowest density at which a strictly jammed state can exist. This RLP state is more ordered than the MRJ state and is extremely fragile (Torquato et al. 2000). In contrast to the concept of random close packing (RCP) (Donev et al. 2004; Torquato et al. 2000), the MRJ state is protocol-independent leading to a mathematical framework for studying



Jamming of Granular Matter, Fig. 16 Force-force correlation functions obtained from 2D experiments. To compute these correlation functions, we compute the average force magnitude, $\langle F(r+r')F(r) \rangle$, acting on a particle. Since the system may be anisotropic, the average over r' must retain the angular information. We contrast data for a system that has been subjected to pure shear, top, with one that has been subject to isotropic compression, bottom

(see part **b** of Fig. 14). The right side of the figure shows a grayscale representation of the data. For the shear case, the correlation function has a roughly power-law decay (to the limits of the system size) for correlations along the strong force chain direction, and a rapid drop off for the transverse direction. For the isotropically compressed case, the correlations are identical in all directions, and decay rapidly (Majmudar and Behringer 2005a)

randomness in hard particle packings. The definition of MRJ does, however, depend on the choice of the order parameter, and further work needs to be done to explore appropriate order parameters.

Isostatic Packings are Marginal

It has become increasingly clear through theoretical analysis and simulations that isostatic packing of frictionless, isotropic particles are marginally stable. Simulations show that the vibrational spectrum of these packings have many soft modes and

that the density of states of zero-frequency modes become non-zero as Point J (which is isostatic) is approached (O'Hern et al. 2003). There is a diverging length scale associated with these vibrational modes, and this length scales as $1/(z - z_{\text{iso}})$ (Wyart et al. 2005a, b). The theoretical explanation for this divergence is rooted in the vanishing degrees of freedom as the isostatic point is approached from the jammed, hyperstatic side (Wyart 2005; Wyart et al. 2005a; Ellenbroek 2007). Stability analysis of the packing of deformable, isotropic grains, also shows that there is a

marginal stability line along which, the pressure of the packing obeys $p/B = (z - z_{\text{iso}})$, (Jaeger et al. 1996b) where p is the pressure and B is the bulk modulus of the packing (Wyart 2005; Ellenbroek 2007). Packings with fewer than the number of contacts specified by this relation are unstable. The question of whether isostaticity and marginality always go hand in hand is an interesting question that is beginning to be explored (Donev et al. 2007; Krzakala and Kurchan 2007).

Simulations and Theory

As discussed in section “Isotropic vs. Anisotropic Stress States”, simulations of deformable, spherical grains (O’Hern et al. 2003; O’Hern et al. 2001) exhibit a special packing fraction, ϕ_c , below which it is impossible to construct a jammed packing, and interestingly, for large systems, ϕ_c approaches the RCP value. Recent theoretical work based on the isostatic nature of Point J (Wyart 2005; Ellenbroek 2007), have provided an explanation for the diverging correlation length and the scaling relation between pressure and the number of contacts. A theory based on a minimum number of contacts needed for *local* stability is the K-core percolation model of Schwartz et al. (2006). This theory focusses on the mixed first-second order nature of the transition at Point J in terms of the order parameter, $\langle z \rangle$, which approaches z_{iso} with an exponent close to 1/2 as $\phi \rightarrow \phi_c^+$, but which is predicted to be zero for ϕ infinitesimally below ϕ_c . The meanfield exponents of this model agree with the exponents associated with Point J in the numerical simulations.

A field theory of jammed grain packings in two dimensions, and close to Point J has been constructed using the generalized stress-based ensemble (section “Statistical Framework of Jamming”), and a fluctuating field related to the Airy Stress function (Ball and Blumenfeld 2002). This field theory (Henkes and Chakraborty 2005), identifies two order parameters associated with the transition at Point J; the Airy stress function and the deviation of the number of contacts from the isostatic value. The field theory predicts a transition with a diverging length scale. Recent work (Henkes and Chakraborty 2008) has focussed on refining this field theory by

comparing its predictions to simulations of frictionless disks (O’Hern et al. 2003).

The stress-based ensemble described in section “Statistical Framework of Jamming” can be used to understand the exponential form of $P(F)$, if one uses the fact that the packings at ϕ_c are isostatic. The starting point of this calculation is the canonical partition function of the stress-based ensemble: $Z(\alpha) = \sum_v e^{-\alpha \Gamma_v}$, where α is the counterpart of the inverse temperature and $\Gamma = \sum_{ij} |r_{ij}| F_{ij}$ (Henkes et al. 2007). At ϕ_c , the spheres or disks are just touching, and therefore, the separations $|r_{ij}|$ can be replaced by the diameter of the grains. The sum over grain configurations, v , therefore, involves a sum over the F_{ij} ’s and the angles of the contact vectors. The isostatic point is special in that there is a one-to-one correspondence between geometry and forces. This means that for a chosen set of $\{F_{ij}\}$, there is only one geometry characterized by a set of contact angles that can be mechanically stable. The partition function then becomes:

$$Z(\alpha) = \sum_{\{F_{ij}\}} e^{-\sum_{ij} \alpha F_{ij}} = \left[\int_0^\infty dF e^{-\alpha F} \right]^{z_{\text{iso}} N / 2} \quad (6)$$

The integral is easily performed, and the result can be used to relate α to the average contact force, $\langle F \rangle$: $\alpha = (z_{\text{iso}}/2) \langle F \rangle$. Since the forces on different contacts are completely independent of each other at this isostatic point, as seen from Eq. (6), it follows that $P(F) \propto e^{-\alpha F} = e^{-z_{\text{iso}} F / (2 \langle F \rangle)}$, a pure exponential. This is a consequence of isostaticity. Away from the isostatic point, the correspondence between geometry and a set of contact forces is no longer one-to-one and distributions will acquire a non-exponential character, in agreement with observations that $P(F)$ of crystalline packings are more Gaussian than disordered packings, as discussed in section “Force Distributions, Length and Time Scales in Jammed States near the Jamming Transition”.

Analysis of simulations of frictionless disks, using this generalized ensemble led to a definitive functional form for the distribution of $\Gamma_m = \sum_{i=1}^m \sum_j r_{ij} F_{ij}$, the pressure of m particles inside an assembly of N grains, integrated over the

volume occupied by the grains (Γ is known as the internal virial). The distribution $P_m(\Gamma_m)$ depends only on $x = N\Gamma_m/\Gamma_N$, where Γ_N is the internal virial of the whole assembly of N grains, and the functional form is (Henkes et al. 2007):

$$P_m(x) \propto x^{\text{ma}} e^{-ax}, \quad (7)$$

where $a = 2 + (\langle z \rangle - z_{\text{iso}})^2$. This form indicates that the distribution would approach a Gaussian with a width which narrows as $\sqrt{m}$, in x space. In the space of the unscaled variable Γ_m , however, the distribution could acquire a non-trivial shape and scaling with m if $\Gamma_N \rightarrow 0$, or equivalently, $\alpha \rightarrow \infty$. Since this is what happens as $\phi \rightarrow \phi_c$, one can expect non-trivial scaling of the pressure distribution. Equation (7) also shows that the exponential tail is maximally stretched at $\langle z \rangle = z_{\text{iso}}$. Evidence for this may appear in the distributions of Fig. 8, where just at the transition, the exponential tail has become extremely extended.

There are many existing models for the exponential distribution of forces. In one view (Corwin et al. 2005b; O'Hern et al. 2001), the exponential distribution is related to the form of the pair correlation function $G(r)$, a function that measures the number of particles separated by a distance r , at small r . Using generic properties of $G(r)$ and the limit where grains are barely compressed, leads to a $P(F) \propto e^{-F^\kappa}$, where the exponent κ depends on the force law. In this approach, the exponential distribution is not related to isostaticity. This point of view was developed through the discussion of the experimental results of Corwin et al. (2005b). A different set of approaches have considered the origin of the unidirectional transmission of forces (force chains) (Cates et al. 1998a, b, 1999) by proposing a new class of constitutive relations arising from constraints on the stress tensor due to geometry of the packings. This approach has a natural connection to the generalized ensemble (Edwards and Blumenfeld 2007; Blumenfeld 2007) and isostaticity (Edwards and Blumenfeld 2007; Tkachenko and Witten 1999; Ball and Blumenfeld 2002). An earlier, heuristic model, the q -model led to unidirectional propagation of forces, and an exponential distribution of contact forces (Coppersmith et al. 1996). More recently,

Snøeijer et al. (2004d) and Tighe et al. (2005b) have predicted force distributions using the force ensemble approach (section “Statistical Framework of Jamming”). The connection between the stress-based ensemble and force chains, away from isostaticity is still being explored.

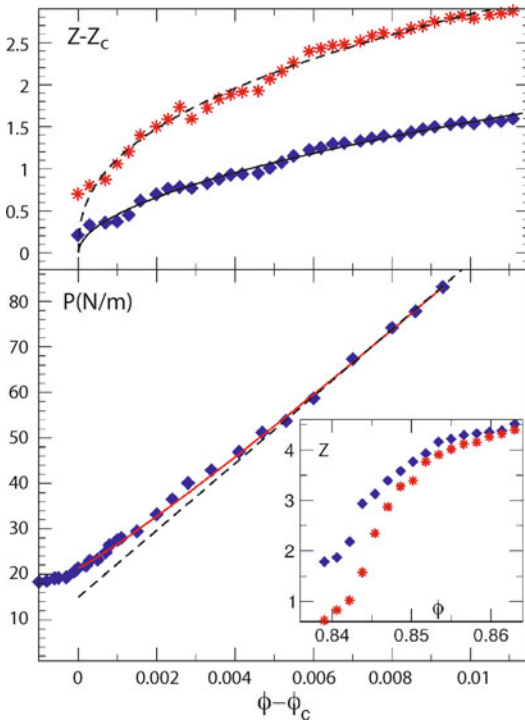
Experimental Observations

Direct experimental investigation of Point J, approached from the jammed side, and the behavior in its vicinity have been more limited than computational and theoretical studies. We are aware of only one experiment by Majmudar et al. (2007) that has directly probed Point-J from the jammed side. This work (Majmudar et al. 2007) has provided detailed experimental data for the mean contact number, Z , and the pressure, P vs. the packing fraction, ϕ_c . Hence, it is possible now to make direct comparison between a physical experiment and theory/model results. In these experiments, photoelastic disks were confined in the biaxial tester discussed above. The photoelastic approach allows the experimental determination of contact forces between pairs of particles or between particles and a boundary.

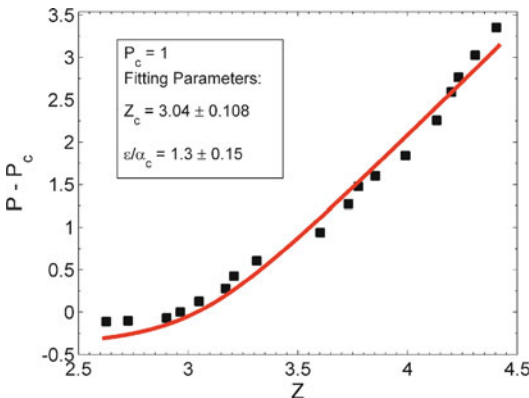
Figure 17 shows results for $Z(\phi)$ and $P(\phi)$. The data for Z show a fairly rapid increase in Z with increasing ϕ , but not a truly sharp discontinuity. However, assuming a reasonable choice of ϕ_c , the data indicate an increase of Z above the critical value which varies as $Z - Z_c \propto (\phi - \phi_c)^\alpha$ with an exponent $\alpha = 0.55 \pm 0.05$. This result is in agreement with the simulation of frictionless grains (O'Hern et al. 2003). The pressure also follows a power-law in $\phi - \phi_c$ with an exponent of 1.1 ± 0.05 , which is in agreement with Silbert et al. (O'Hern et al. 2003). Finally, it is possible to compare to the stress-ensemble predictions of Henkes and Chakraborty by eliminating α in their predictions for $P(\alpha)$ and $Z(\alpha)$ to obtain an expression for $P(Z)$. The data, Fig. 18, are also in reasonable agreement with this prediction.

Future Directions

From the combined experimental, theoretical, and simulation studies of the last decade, a picture of



Jamming of Granular Matter, Fig. 17 Data for the pressure and for the mean contact number per particle, Z vs. ϕ . The inset shows that Z vs. ϕ over a larger range than the top part of the figure. Data including rattlers as shown by asterisks, and data without rattlers by diamonds. Note that Z rises rapidly but not discontinuously at jamming. Power-law fits of P and $Z - Z_c$ vs. $\phi - \phi_c$ above jamming and for reasonable ϕ_c show expected exponents of 0.55 ± 0.05 for $Z - Z_c$ and 1.1 for P (Majmudar et al. 2007)



Jamming of Granular Matter, Fig. 18 Data of Majmudar et al. for P vs. Z showing the generally good agreement with the predictions of Henkes and Chakraborty (Majmudar et al. 2007)

the nature of jamming in granular matter is beginning to emerge, although many questions remain. In our discussion, we distinguish jamming/unjamming under isotropic and anisotropic stress conditions. Many recent simulations have considered the isotropic approach to Point J. A number of experiments have explored jamming/unjamming, although most of these involved the succession of failures that occur under shear and away from Point J, which corresponds to processes with a heuristically ‘first-order’ character. We believe that it is important to distinguish these various cases. To our knowledge, no one has considered the approach to Point J along an anisotropic stress path.

There are clear indications of heterogeneities in granular matter. These have both a spatial and a temporal aspect, and they become increasingly important with the approach to jamming. They have been identified on both the fluid-like and jammed side of the transition.

One aspect of these heterogeneities is concerned with forces and their transmission. A clear manifestation is in force chains, which can show strong correlations in the sheared state, but very short range correlations in the isotropic stress state. In dynamic processes, force chains continually rearrange, leading to strong force fluctuations. Although force chains are clearly visible in a variety of 2D experiments that are carried out above jamming, incipient stress chains have been observed in simulations of hopper flow on the fluid-like side (Ferguson and Chakraborty 2007), and there is evidence of arch formation and stress chains in experiments studying jamming in hopper flow (To 2005; Zuriguel et al. 2005; Easwar n.d.). An open question concerns the role that such structures may play if Point J is approached along a path of anisotropic stress.

A different type of heterogeneity in granular flows is related to the mobilities of grains (Keys et al. 2007; Dauchot et al. 2005). This situation is similar to heterogeneities in supercooled liquids.

The analogies between jamming and thermal phase transitions prompts questions about the extent of the similarities between the two. For instance, is there an order parameter associated with the transition? Studies of the special type of

jamming at Point J suggest that pressure and the deviation of the number of contacts from the isostatic value are the two, possibly coupled, candidates for the order parameter.

The generic jamming/unjamming transition that takes place in the presence of non-zero shear stress is characterized by intermittent dynamics and is reminiscent of trap-like dynamics, where the shearing causes the system to “hop” from one jammed state to another and jamming occurs when the average time scale for exploring all the traps diverges (Behringer et al. 2008; Monthus and Bouchaud 1996). The framework of soft-glassy-rheology (Sollich 1998) provides an approach to calculating the stress response of granular packings approaching jamming. In this picture, the jammed state is an intrinsically non-equilibrium state, which exhibits aging, meaning a slow evolution of its properties with time. The issues raised here are much the same as those arising in the context of the glass transition, and involve understanding the relation between fluctuations and response (Bouchaud et al. 1996), through the definition of an effective temperature. This is an area of active research (Song et al. 2005a, b; Potiguar and Makse 2006; Ono et al. 2002; O’Hern et al. 2004).

Understanding the jamming of non-spherical grains is much less advanced than that of spherical grains. In this regard, the geometrical approach of Torquato and Stillinger (Donev et al. 2007) is being applied to non-spherical grains. Experiments have probed the issue of isostaticity in non-spherical grains (Desmond and Franklin 2006; Man et al. 2005; Blouwolff and Fraden 2006). The stress-based ensemble described in this article is a promising approach for analyzing these issues.

In the context of frictional and frictionless packings, a question that needs to be addressed is what aspects of the jamming transition are sensitive to the presence of friction. Simulations and theories of jamming have mainly focussed on frictionless grains. The statistical ensemble approaches, however, are general and provide an avenue for a unified framework.

These observations raise many questions:

1. How are stress chains related to the the mobility of grains? Since force chains tend to lock grains in place, it may well be that there is anti-correlation between force chains and mobility.
2. Is there a basic dynamical principle leading to the occurrence of stress chains, or are they more strongly influenced by geometry?
3. What if any, is the relationship between the length and time scales on the jammed side to those observed on the flowing side?
4. Are incipient chains on the fluid-like side responsible for jamming as the transition is approached? Is jamming caused by a divergence of the lifetime of these chains?
5. Is there an extension to jamming in the presence of shear? That is, how does the path in P - τ space affect jamming?
6. What is the nature of jamming for nonspherical particles, for systems with a broad range of particle sizes, or for particles that interact with cohesive forces?

The advances in experimental techniques which have led to the measurement of grain-level forces, has been a tremendous boon for theorists. Simulations have led to detailed descriptions of fluctuations which provide means for testing theoretical frameworks. The recent advance in the statistical ensemble approach to jamming, the geometrical characterizations of packings of rigid grains, combined with the detailed experimental and simulation studies, is expected to answer many of the remaining questions and lead to a fuller understanding of the phenomenon of jamming.

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Rigidity Percolation and Frictional Jamming

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Article Outline

Glossary

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Bibliography

Glossary

Force chain Heterogeneous stress in granular packings with localized force transmission along one-dimensional structures.

Friction Property of mechanical contacts that support tangential loading due to microscopic asperities.

Isostatic The state of a packing where the number of degrees of freedom exactly balances the independent constraints.

Jamming Transition to rigidity in granular materials from a liquid-like state to a state that supports shear stresses.

Percolation The study of the connectivity of a structure, such a particle packing, via connectivity clusters, including the onset of a spanning connectivity cluster defining the location of a percolation transition.

Rigid cluster Part of a packing where the number of independent constraints is greater or equal to the number of degrees of freedom; region that supports mechanical load.

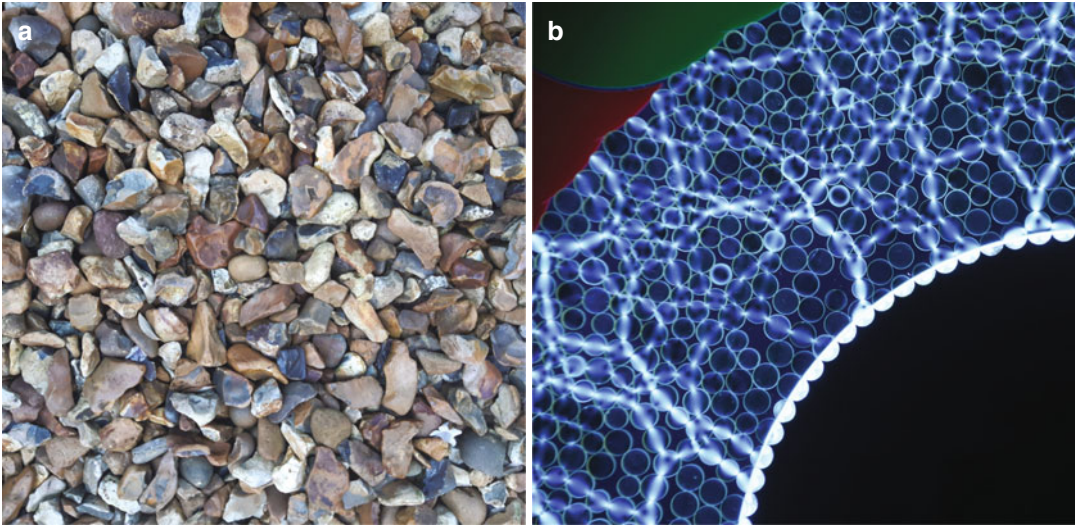
Spanning rigid cluster Rigid cluster that spans the size of the system, equivalent to attaining macroscopic rigidity, i.e., being jammed.

Definition of the Subject

Frictional jamming in granular materials is the transition between a state cannot support an applied stress and so yields or flows, and one that can. For example, in sand on a well-travelled beach, an old footprint remains frozen in the sand until the stress applied by a new step causes it flow into new shapes.

Introduction

Granular materials are ubiquitous both in nature and in manufacturing. They span a range of composition, from sand to pebbles (see Fig. 1a) to grains to coal to pharmaceuticals, and a range of sizes from the finest powder in pharmaceutical processing to the loose icy gravel that makes up small asteroids (Kleinhans et al. 2011; Bogdan et al. 2020). Despite differences in composition and size, what these materials have in common is that they are made of discrete, solid units that are interacting with each other primarily through (mostly) repulsive contact forces, and that they are sufficiently large for thermal fluctuations to be irrelevant. Related, but different, materials include colloids and dry foams and cells in tissues. Colloids are typically smaller in size such that thermal fluctuations may be significant and interact via longer-ranged attractive polar forces and depletion forces (Fernandez-Nieves and Puertas 2016). Dry foams and cells in tissues are sufficiently deformable to create confluent arrangements



Rigidity Percolation and Frictional Jamming, Fig. 1 Examples of frictional granular materials. (a) The gravel in your front yard hides a secret: Mechanics and stress transmission in such a jammed frictional granular packing are highly complex. Image is from the author's

front yard. (b) Frictional granular material made from photoelastic disks imaged between cross-polarizers, showing stress transmission along force chains. Image courtesy of Farnaz Fazelpour and Karen Daniels

without the interstitial free volume characteristic of a packing of nondeformable granular particles (Alberts et al. 2018).

Despite the interactions driving granular materials being primarily contact forces, they still exhibit a range of different phases from gaseous to fluid-like, or unjammed, to solid-like, or jammed, as they are driven by nonequilibrium stresses at different packing fractions, for example, with the latter two phases characterized by the jamming phase diagram (Liu and Nagel 1998; Ciamarra et al. 2010). Moreover, granular packings exhibit a wealth of interesting, more detailed phenomena from hysteretic flows (Daniels and Behringer 2005; Silbert et al. 2001; DeGiuli and Wyart 2017) to force-chains (Cates et al. 1998; Majmudar and Behringer 2005) to avalanches (Daerr and Douady 1999; Staron and Radjai 2005; Pudasaini and Hutter 2007). As for hysteretic flows, once a packing begins to flow above some critical value of applied shear stress, to stop the flow, one must impose a shear stress less than the critical value to generate the flow. Force chains, or chain-like structures with branchings in the force map for those forces greater than the average force, emerge in jammed packings.

Avalanches are large-scale rearrangements of a packing initiated by the motion of just several particles and can be difficult to predict.

While friction is typically part-and-parcel to granular packings, given the complications of hysteretic phenomenon, some theoretical efforts, at least in the physics community, focused on frictionless granular packings. Such packings also exhibit a jamming transition, or a transition from fluid-like behavior to solid-like behavior as its packing fraction is increased as evidenced by the elastic moduli going from zero to non-zero (Ohern et al. 2003). Frictionless granular packings also exhibit force-chains and avalanche-like behavior, at least near the jamming transition (Tighe et al. 2010; Xu et al. 2010; Bassett et al. 2015; Olson Reichhardt and Reichhardt 2010). At the onset of jamming occurs when the packing becomes mechanically stable to perturbations, much progress has been made in understanding the nature of the frictionless jamming transition by analyzing the mechanical constraints of the system (Tighe et al. 2010; Wyart et al. 2005). When the degrees of freedom outweigh the constraints, the packing is unjammed. In the opposite case, the packing is jammed and when there is a balance

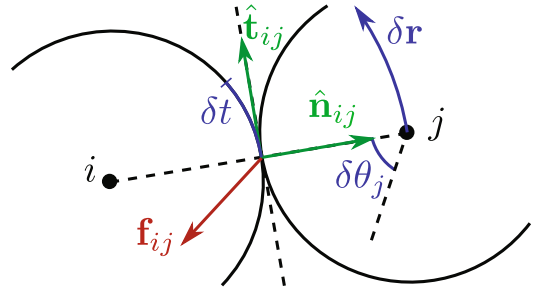
between the two, the system is isostatic, or at the boundary between the two phases. As a consequence of such an approach, consensus has been reached that the frictionless jamming transition is mean-field-like and has a mixed nature in terms of a discontinuous onset of average coordination number from zero, accompanied with several diverging correlation lengths, typically suggestive of a continuous phase transition in systems in thermal equilibrium (van Hecke 2009). The focus of this review is to determine if such findings carry over to frictional granular packings, which are more generic in nature. After doing so, we will conclude with a discussion of how our theoretical approach relates to other theoretical approaches to frictional jamming, most notably, theoretical approaches to understand the phenomenon of shear jamming as well as give the reader a glimpse into related problems and open questions.

Friction in Granular Materials

Frictional Contacts

Friction is an emergent property of solid materials in which microscopic interactions give rise to an effective resistance to transverse load. At the microscopic scale of a single contact between two particles, microscopic creeping and slipping events at the rough interface allow for the system to support tangential loading, up to a threshold that depends sensitively on the interface properties and compression. At the simplest level, in *Coulomb friction*, this threshold is approximated as proportional to the normal compression force, i.e., the system supports tangential loading for $|f_t| \leq \mu f_n$, where μ is the static friction coefficient. Further tangential motion also induces resistance and is then modelled by a dynamical friction coefficient.

While frictional contacts are complex and the subject of active research effort (Müser et al. 2017), basic Hertz-Mindlin contact theory (Mindlin 1949), captures the qualitative features of a frictional contact law: For two spherical particles of radius R_1 and R_2 , respectively, as shown in Fig. 2, in contact with a deformation depth δ , with normal f_n and tangential force f_t are given by:



Rigidity Percolation and Frictional Jamming, Fig. 2 Geometry and local coordinates around a frictional contact. Particles i and j share a contact point with local normal and tangential vectors $\hat{n}_{ij}$ and $\hat{t}_{ij}$. The infinitesimal motion at the contact can be decomposed into a translational component $\delta \mathbf{r}$ and rotational components $\delta \theta_i$ and $\delta \theta_j$

$$\begin{aligned} f_n &= k_n \delta^{3/2}, & df_t &= f_n dt \text{ if } |f_t| \leq \mu f_n, \\ f_t &= \mu f_n \text{ otherwise,} \end{aligned} \quad (1)$$

with dt denoting the tangential sliding increment $dt = \delta \mathbf{r} \cdot \hat{t}_{ij} - (R_i \delta \theta_i + R_j \delta \theta_j)$. The normal stiffness k_n is given by Hertzian elastic deformation theory (Hertz 1881; Johnson 1982; Johnson 1987) with $k_n = \frac{4}{3} \sqrt{RE^*}$, where $1/R = 1/R_1 + 1/R_2$ and $E^* = 2E/(1 - \nu^2)$ with E , the Young's modulus, and ν , the Poisson ratio. The tangential force has a differential form since for every tangential sliding increment dt , the force increases (or decreases) up to the Coulomb threshold, and then it remains constant during the sliding phase. More elaborate theories which include either a different dynamic friction coefficient or contact laws that incorporate liquid bridges have been developed as well (Barber and Ciavarella 2000; Ciavarella et al. 2019).

Experiments

Experiments on frictional granular materials span a range from industrial research, where the focus is on precise modelling of, e.g., a production environment (see Coussot 2005), to more abstract setups, which are more useful to understand jamming (Jaeger et al. 1996; Duran 2012). It is these latter ones we will focus on here. They include silica beads (Mueth et al. 1998), dense suspensions (Brujić et al. 2003), and most importantly

for studies of frictional jamming, photoelastic disks (Amon et al. 2017).

Silica (i.e., SiO_2 , or quartz) beads consist of grains that are spherical and monodisperse to the best experimental precision, with known material properties. Other controlled experimental conditions, such as humidity control are also frequently used to make experiments reproducible. Silica beads have been used extensively to understand the flow properties of granular materials, e.g., in a hopper or tilted plane/avalanche setup, or in various types of explicit rheological setups, such as a Couette geometry with differentially rotating cylinders (Forterre and Pouliquen 2008). Such three-dimensional setups are an excellent approximation of industrially relevant flows, but it is very difficult to know their internal structure and forces. In addition to explicit rheometers and sensors at specific points in the flow (Gardel et al. 2009), X-ray tomography has been used to determine the packing of such beads (Weis and Schröter 2017). This method can, however, only give limited dynamical information and no force information. To understand the properties of static packings, on other hand, earlier experiments measured the forces exerted on boundary particles (Mueth et al. 1998; Liu et al. 1995).

Better imaging of three-dimensional granular materials can be achieved by immersing transparent particles in an index-matched fluid. Then confocal imaging together with laser-sheet illumination can reveal the internal structure of the system (Amon et al. 2017). This method has been applied to both macroscopic (Dijksman et al. 2012) and microscopic granular packings. For microscale setups of deformable droplets, forces can be determined from inverting the deformation at the contact. Fluorescent markers can help distinguish membranes in contact with each other from a free interface, and so allow for an accurate measure of the contact area and, hence, the interaction forces (Brujić et al. 2003; Clusel et al. 2009). Dynamically, these setups are more accurately described as dense suspensions: While their static properties, e.g., the packing structure and force distributions, are equivalent to either frictional or frictionless packings, viscous dissipation in the surrounding liquid is crucial to their

rheological properties. In particular, the issue of shear-thickening in such dense suspensions has attracted a lot of attention in recent years (Brown and Jaeger 2009; Clavaud et al. 2017; Royer et al. 2016; Wyart and Cates 2014). We will address the interaction between shear thickening and frictional rigidity in the concluding section.

An accurate mechanical *and* dynamical picture of two-dimensional granular packings with no surrounding fluid can be uncovered by using photoelastic disks. Cylinder-shaped particles made from a photoelastic material are arranged in a flat packing and are then imaged between cross-polarizers. Contact deformations induce stresses in the material, leading to photoelastic fringes that can be imaged (see Fig. 1b). One can then use Hertzian contact theory to invert the fringe pattern to obtain the contact forces (Majmudar and Behringer 2005; Majmudar et al. 2007). In practice, it took the best part of a decade to optimize this experimental setup: Difficulties include, but are not limited to, nonlinear elastic interactions necessitating solving the inverse problem iteratively for a full packing, and minimizing friction with the bottom plate of the setup (e.g., using an air table) (Daniels et al. 2017) (see Fig. 1b). Rheological measurements on such photoelastic setups are done in the quasistatic limit, by applying step-strains at the boundary in different geometries, with a focus on a pure shear setup where one direction is compressed while the perpendicular direction expands (Bi et al. 2011). Photoelastic disk experiments have given us the only data sets to date on the full set of forces in macroscopic frictional packings with dry solid friction at the contact. These forces can then be tracked over time to obtain information about the dynamics of the packing.

Numerical Models

Simulating frictional granular materials is not an easy task. Unlike for frictionless materials, contact interactions are not conservative, i.e., they do not derive from a potential. This precludes using energy minimization protocols to generate frictional packings, and instead full dynamical simulations are nonnegotiable.

The first simulations of frictional granular matter by Cundall and Strack (1979) were a direct

implementation of the Hertz-Mindlin theory of frictional contacts for two-dimensional cylinders. The interactions between such cylinders are to first order harmonic, i.e., $f_n = k_n \delta$, instead of $f_n = k_n \delta^{3/2}$ since there is a contact line instead of a contact point. More sophisticated models of the frictional contact abound in the engineering literature (Wriggers and Nackenhorst 2006). This type of direct simulation is referred to as *molecular dynamics* (MD) in the physics literature, while it is known as the *discrete element method* (DEM) in engineering. In addition to the contact forces, such simulations are both driven through externally applied shear, and necessarily also include dissipation, either at the contacts or with a surrounding bath. Closely related models include a surrounding liquid for modelling dense suspensions, though usually only through effective viscous pair forces and not a full fluid model. While there are a number of very detailed DEM simulation tools in the engineering and soil mechanics literature (see Wriggers and Nackenhorst (2006) for a review), we focus on the minimal model ingredients here.

Schematically, the equations of motion for a granular MD simulation of two-dimensional, disk-like particles (i.e., real-world cylinders) are given by the force and torque equations:

$$m_i \ddot{\mathbf{r}}_i = \sum_{\langle ij \rangle} [\mathbf{F}_{ij}^c + \mathbf{F}_{ij}^{\text{diss}}] - \zeta \dot{\mathbf{r}}_i \quad (2)$$

$$I_i \ddot{\theta}_i = \sum_{\langle ij \rangle} \mathbf{r}_{ij}^c \times [\mathbf{F}_{ij}^c + \mathbf{F}_{ij}^{\text{diss}}] - \zeta_{\text{rot}} \dot{\theta}_i. \quad (3)$$

Here, $\mathbf{F}_{ij}^c = F_{ij}^n \hat{\mathbf{n}}_{ij} + F_{ij}^t \hat{\mathbf{t}}_{ij}$ and for round particles, only the tangential force contributes to the torque. The pair dissipation forces usually take the simple form $\mathbf{F}_{ij}^{\text{diss}} = -\zeta_{\text{pair}} (\dot{\mathbf{r}}_j - \dot{\mathbf{r}}_i)$. For a simple harmonic contact model, this corresponds to a spring and a dashpot in parallel, i.e., a Kelvin model, in both normal and tangential directions.

To explore frictional jamming, such MD simulations have been paired with Lees-Edwards boundary conditions (Allen and Tildesley 2017), where a simple shear is imposed by shifting the top and bottom of periodic boundary conditions

with strain rate $\dot{\gamma}$. Alternatively, simulations can be run with a constant applied (shear) stress σ by applying a force profile to the simulation (Heussinger 2013; Grob et al. 2014). Another protocol, inspired by experiment, is to incorporate gravitation and generate a heap of sand simulation, and study its instability to tilting or rotating the support (Staron and Radjai 2005). A final simulated protocol is to generate states by controlling the system pressure in a viscous environment (Shundyak et al. 2007; Somfai et al. 2007), thereby explicitly sampling states at very low pressure and, hence, near frictional jamming.

MD simulations of frictional particles are computationally expensive and, in particular, for very hard grains (as is appropriate for, e.g., silica beads or sand), time steps need to be very small to resolve individual collisions. At the same time, in the plastic deformation regime, time scales for significant flow are very large. This separation of time scales has given rise to collision-based algorithms for frictional granular packings: The contact dynamics algorithm (Jean 1999; Radjai and Richefeu 2009) combines a well-defined collision protocol with an iterative algorithm to respect the Coulomb criterion and instantaneous force balance, and it has been used to simulate avalanches (Staron and Radjai 2005). Related models are used for lower density granular flow (Bannerman et al. 2011) and in computer animation (Bell et al. 2005). Computational speedup comes at the expense of a realistic contact model, however.

Frictional Jamming

Given the difficulties in obtaining both forces and dynamics in frictional granular packings, earlier experimental work centered on questions regarding the lowest attainable density of packing, i.e., *random loose packing* (Onoda and Liniger 1990) and tests of the Edwards volume ensemble (Edwards and Oakeshott 1989; Blumenfeld and Edwards 2009; Puckett and Daniels 2013). Additionally, dense, frictional granular packings revealed two distinct phases: a fluid-like phase with the packing flowing in response to an applied perturbation at lower densities and a solid-like phase with no flows at higher densities. Later, an

additional shear-jamming transition where the system solidifies in response to a finite perturbation was discovered (Bi et al. 2011). The boundary between these two phases is otherwise known as the frictional jamming transition. Characterization of this transition started in earnest around the turn of the millennium with simulations using both variants of the molecular dynamics approach introduced above (Silbert et al. 2002; Silbert 2010; Ciamarra et al. 2011; Hatano 2007) and contact dynamics (Radjai et al. 1996). In parallel, simulations on granular flows that are not jammed continued (Forterre and Pouliquen 2008).

Simulations of slowly sheared packings in two dimensions established a hysteresis loop (Ciamarra et al. 2011; Hatano 2007) between unjammed packings at low packing fractions (typically $\phi < 0.74$) and jammed packings at higher density. These simulations also established that the jamming packing fraction (as variously defined by the protocol) strongly depends on the friction coefficient μ , with higher μ corresponding to lower packing fractions (Silbert 2010). Other simulations (Shundyak et al. 2007; Somfai et al. 2007) sought to formalize this result and focused on creating frictional packings through an overdamped equilibration mode in a stress-controlled ensemble. Interestingly, experimental two-dimensional packings of photoelastic frictional disks fall within the range of simulated results (Majmudar and Behringer 2005). These findings are in stark contrast with frictionless packings not exhibiting such hysteresis and having well-defined transition point as a function of density, or packing fraction.

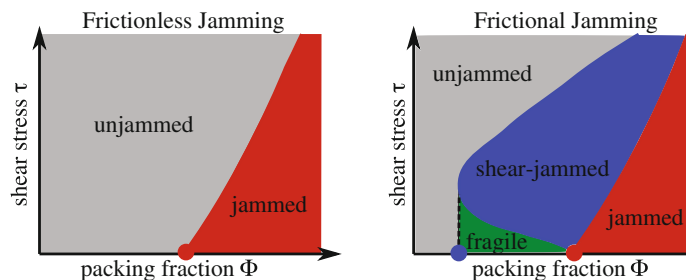
The absence of a well-defined transition packing fraction, or contact number, then led to exploring the local structure of packings. First, the

analysis of the anisotropy of the local force and contact network (Peters et al. 2005; Tordesillas et al. 2010; Walker et al. 2011) led to the development of shear jamming. Shear jamming (Bi et al. 2011; Vinutha and Sastry 2016; Peters et al. 2016; Wang et al. 2018; Zhao et al. 2019) starts from the empirical result that an initially unjammed frictional packing will frequently jam when a shear stress is applied at constant volume fraction. When under shear stress, the internal stress state of the system becomes necessarily anisotropic with a growing correlation length in the principal stress direction (Baity-Jesi et al. 2017). At a microscopic level, this corresponds to force chains orienting themselves along the principal stress direction. This divides the force network into “strong forces” and “weak forces.” The strong forces forming chains was first highlighted by Radjai et al. (1998) more than two decades ago. The shear jamming measure thresholds the contact network to retain only the above-average forces $f > \langle f \rangle$, where the average is a spatial average over the given configuration. The resulting network can either fully percolate, percolate in one direction only, or not percolate at all. Shear jamming classifies the states that can be obtained in this manner as *unjammed*, *shear-jammed*, and *fully jammed*. In the phase diagram proposed in (Bi et al. 2011) (Fig. 3), the reentrant nature of the jamming line in axes of packing fraction and applied shear stress becomes apparent. Again, this result should be contrasted with the frictionless case where there is no reentrant effect.

As for the second local structure approach in terms of analysis of the number of sliding contacts (Shundyak et al. 2007; Henkes et al. 2010), we will turn to constraint counting, which is at the

Rigidity Percolation and Frictional Jamming,

Fig. 3 Jamming phase diagram as a function of packing fraction and shear stress for frictionless and frictional packings. (The image is a redrawing of the phase diagram proposed in (Bi et al. 2011))



heart of rigidity percolation, initially constructed for frictionless systems. In the last section, we will comment on the complementarity of the two approaches.

Rigidity Percolation

Maxwell Constraint Counting

Let us begin briefly with percolation before addressing rigidity percolation. Percolation considers a spatially embedded graph of vertices (particles) and edges (bonds), and asks the simple question: Does the graph contain a spanning cluster, i.e., a subgraph of vertices connected via bonds that span the entire length of the embedding? *Connectivity* or *bond percolation*, the original and best-known form of percolation, simply requires that the graph of the bonds defined by particle-particle contacts leads to a spanning cluster (Stauffer and Aharony 2018). This is necessary for a jammed packing, but it is by no means sufficient! For example, a one-dimensional chain of connected particles is mechanically unstable due to buckling under compression; however, it forms a bond-percolated system.

To gauge the mechanical stability of a system, rigidity percolation then asks the following question: Is there a spanning, mechanically rigid cluster in the system? As we will detail below, within the constraints of a quasistatic system with infinitesimal displacements, this question is equivalent to (or at least strongly correlated with) the question of whether or not a system is jammed.

To mentally unpack rigidity percolation, we need to step back to the time of James Clerk Maxwell (1831–1879). In the middle of the Victorian industrial age, it became important to understand the mechanical stability (or lack thereof) of iron frames to construct, for example, railway bridges and stations. Inspired by these applications, in a pair of seminal papers (Maxwell 1864, 1870), Maxwell developed the idea of *constraint counting*, where rigidity is acquired by introducing a sufficient number of constraints for the degrees of freedom in the system.

Let us illustrate Maxwell constraint counting for a packing of frictional particles in d

dimensions. Each particle has d translational degrees of freedom and $\frac{1}{2}d(d-1)$ rotational degrees of freedom, leading to a total of $N\frac{1}{2}d(d+1)$ degrees of freedom for a packing composed of N particles. To constrain the motion along these degrees of freedom, we use the forces between particles: In the idealized situation of a packing with infinite friction coefficient $\mu = \infty$, regardless of the orientation of the contact surface, the force can point in any direction. We have also neglected the restrictions imposed of a purely compressive force. Under these circumstances, the interparticle force has d independent components which impose d constraints on the motion of the packing. Due to every contact being shared between two particles, the total number of contacts is given by $N_c = N\frac{z}{2}$, where z is the mean number of contacts between particles. When we have constrained the packing sufficiently, the full system acts as a rigid body, but it will still retain d translational and $\frac{1}{2}d(d-1)$ global rotational degrees of freedom. Therefore, we need to fix only exactly $(N-1)\frac{1}{2}d(d+1)$ degrees of freedom through our constraints. Then by constraint counting, the packing is rigid if there are enough constraints, i.e., if $Nd\frac{z}{2} \geq (N-1)\frac{1}{2}d(d+1)$ or after some rearrangements,

$$z \geq (d+1) - \frac{1}{N}(d+1). \quad (4)$$

The packing is *isostatic* at $z_{iso} = (d+1)(1-1/N)$ when we have exactly equal number of constraints and degrees of freedom. It is *hyperstatic* or *overconstrained* when there are more constraints at larger $z > z_{iso}$, and it is *hypostatic* or *underconstrained* when there are not enough constraints at $z < z_{iso}$. We will mainly focus on the case $d = 2$ below, where every particle has two rotational and one translational degree of freedom, i.e., three in total. Every contact provides two constraints, one in the normal direction and one in the tangential direction, and we also have three global degrees of freedom. The isostatic point is then given by $z_{iso} = 3(1-1/N)$.

Frictionless isostaticity for spherical particles is the simplest case exhibiting a jamming transition (Ohern et al. 2003; Wyart et al. 2005; van

Hecke 2009). Since for a frictionless spherical particle, orientation is irrelevant, only its d translational degrees of freedom are pertinent. At the same time, interparticle forces are necessarily along the surface normal at the contact point. Since then only their magnitude is variable, not their direction, every contact only contributes one constraint. However, the packing still retains $\frac{1}{2}d(d+1)$ global translational and rotational degrees of freedom. The frictionless packing is rigid if there are more constraints than degrees of freedom, i.e., if $N\frac{z}{2} \geq Nd - \frac{1}{2}d(d+1)$ or after some rearrangements,

$$z \geq 2d - \frac{1}{N}d(d+1). \quad (5)$$

In particular, in two dimensions, we have $z_{iso} = 4 - 6/N$. This z_{iso} is observed in simulations (Ohern et al. 2003), even the $1/N$ correction (Dagois-Bohy et al. 2012; Goodrich et al. 2014). We will return to address particles with both translational and rotational degrees of freedom in the next section.

Laman's Theorem

Maxwell constraint counting has obvious weakness: In addition to the assumption of uncorrelated, or independent, constraints, which breaks down, e.g., for crystalline packings, it only takes into account z , the *mean* number of contacts in the packing. In other words, Maxwell constraint counting is a mean field type approximation. For instance, any small disconnected part of the packing cannot be rigid with respect to the rest of it, no matter how many extra contacts exist between particles of the main packing. This issue is well known in granular packings where “rattlers,” that is particles that have either no or few contacts, are routinely excluded from constraint counting (Ohern et al. 2003). However, there is no guarantee that removing rattlers (even recursively) validates the mean field approximation.

These weaknesses can be overcome by using graph theory. To go from a packing to a graph, we map every particle of the packing to a vertex, and every contact to one or more edges between the vertices. While we lose information of the positions

of the particles, we gain information of the interdependency of constraints, or which constraints are redundant or not. In the absence of friction with only normal forces between particles, the combinatorial Laman's theorem (Laman 1970) gives the necessary and sufficient conditions for the rigidity of such a graph extracted from a two-dimensional, generic packing, where generic translates to the absence of any underlying spatial symmetries in the packing. We state here the more user-friendly formulation due to Tay (1993).

Theorem: *The graph G containing v vertices and e edges is infinitesimally rigid if and only if every subgraph G' , with its own v' vertices and e' edges, satisfies $e' \leq 2v' - 3$.*

The graph is isostatic when $G = G'$. This theorem is very powerful in that it relies purely on a combinatorial approach. Yet, in practical terms, counting the number of edges in every subgraph, which scale exponentially in the number of components (vertices and edges), is computationally cumbersome. This is where a reformulation of Laman's theorem implemented via the pebble game will come in handy.

Unfortunately, the obvious, three-dimensional extension of Laman's theorem guaranteeing sufficiency is not possible, given several counterexamples. However, Tay's theorem (Tay 1984) is a three-dimensional extension of Laman's theorem applied to body-bar graphs representing rigid bodies, each with six degrees of freedom, connected by bars. With such graphs, the counterexamples to the three-dimensional version of Laman's theorem do not exist. In addition to Tay's theorem, there exist linear algebraic approaches to determining whether or not a system is rigid, such as computing the rank of the rigidity matrix (Pellegrino and Calladine 1986). These linear algebra approaches can be implemented in any dimension, though computing the rank of a matrix can also be computationally intensive. We describe an application of the latter and its relation to the pebble game below.

The Pebble Game

The basic notion behind the pebble game is to apply Laman's Theorem recursively by adding

contact edges to the graph one at a time until we achieve the maximal subset of independent edges (Jacobs and Hendrickson 1997; Lee and Streinu 2008), i.e., all the contacts that can be added without introducing redundancy. Keeping track of which edges are independent or not is, therefore, the important part of the game. Once this maximal subset has been identified, we can determine whether the graph is rigid or not. The pebble game can also be used to decompose the graph into rigid clusters.

We begin with an outline of the (2, 3) pebble game, as shown for a sample frictionless packing in Fig. 4. Here 2 denotes the degrees of freedom at a vertex and 3 denotes the number of trivial global zero modes. As shown in panel 2, we assign two pebbles representing degrees of freedom to each vertex and convert each contact into a constraint edge.

We proceed by sequentially adding bonds to the graph by moving pebbles from the vertices onto the edges, thereby identifying these edges as independent constraints. For a given edge, the search for unassigned pebbles begins at the incident vertices, and once a pebble is found, we assign a direction to the edge, away from the vertex that is the origin of the pebble. Due to the three global degrees of freedom, we need to execute a successful pebble search an additional three times (for a total of four) before implementing the first pebble assignment to the edge. Expressed at a set of rules, we have:

Rule 1. No more than two pebbles can be present on any vertex.

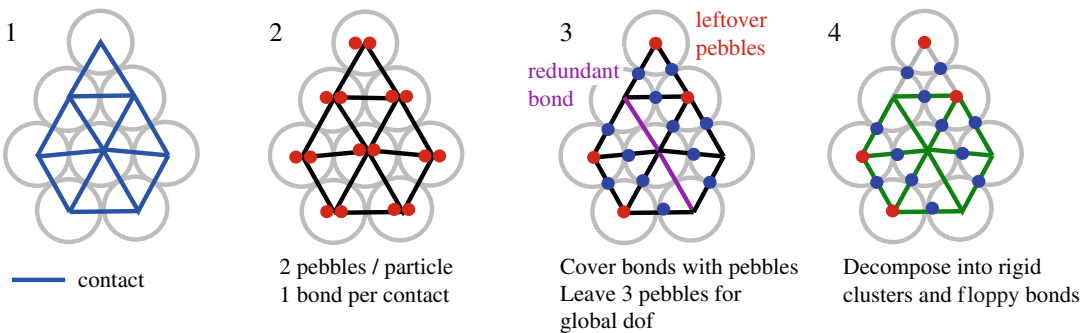
Rule 2. A directed bond is accepted into the directed network when at least a total of four pebbles are present at the two vertices defining the bond.

Eventually, the search for pebbles at the incident vertices will fall short. Then we execute a depth-first directed graph search for unassigned pebbles at other vertices backwards along the directed bonds that are already part of the graph. Once enough pebbles are found at the two ends of an edge, one of them is reassigned to the edge, as before. Algorithmically, we proceed as follows:

Move A. A pebble found via depth-first search starting at vertex v is moved along the directed path while reversing the arrows until reaching v .

Move B. If a directed bond is accepted into the directed network via Rule 2, then the found pebble is reassigned to an edge and is no longer at play.

The (2, 3) pebble game is played until all edges in the graph have been considered, as shown in panel 3 of Fig. 4. This algorithm ensures that the edges accepted into the directed graph map to independent constraints. If there are more than three pebbles that have not been reassigned to an edge, then the graph is floppy.



Rigidity Percolation and Frictional Jamming, Fig. 4 The (2, 3) pebble game. Step 1: A frictionless packing is mapped to a graph with two pebbles on each vertex. In step 3, the two pebbles per particle are placed on

bonds where possible using the pebble game, leaving leftover pebbles and redundant bonds (purple). In step 4, the graph is decomposed into rigid clusters (green) and floppy bonds (gray)

Conversely, if there are three pebbles left over and bonds that have not been accepted into the directed graph, then these correspond to redundant edges (purple). Note that such edges are not necessarily unique since they may change depending on the order in which the edges are considered. A graph can both be floppy and contain redundant edges, as some pebbles, e.g., at poorly connected vertices are inaccessible via the directed search. The algorithm time for the pebble game typically scales linearly with the number of edges in the graph.

We can also use the (2, 3) pebble game to identify the rigid clusters, i.e., the subgraphs that have $2v - 3$ independent edges. Two vertices v_1 and v_2 in G that are linked by bond b are mutually rigid if a search for a free pebble at both ends comes up short. Intuitively this is because both are part of the same rigid cluster with its exactly three global degrees of freedom, so that no extra pebbles are available. However, if an extra pebble can be found, they are either part of two distinct rigid clusters, or one or both are in floppy regions. Making use of the fact that the directed graph pebble search necessarily traverses the rigid cluster before coming up short, we can quickly (at order of number of rigid clusters) mark particles and bonds as mutually rigid or floppy. If there is a redundant edge, the search for a free pebble has failed, and it therefore necessarily belongs to a rigid cluster, and more specifically the same cluster as the two vertices at either end. One can also identify over-constrained clusters in which redundant edges are added, and which each correspond to a state of self-stress. Interestingly, while the number of redundant edges is independent of the way in which the graph is “grown,” the labeling of the redundant edges is not independent of this process, i.e., a different ordering of edges tested leads to different redundant edges.

The (2, 3) pebble game can be generalized to a (k, l) pebble game. For instance, implementation of Tay’s theorem translates to a total sum of seven $(k + 1)$ free pebbles at either end of the edge, and if there are more than six (l) pebbles that have not been reassigned to an edge, then the graph is floppy.

Rigid Clusters and Nature of the Rigidity Transition

Now that we can map out the rigid clusters in a packing, we can circle back to the nuts and bolts of rigidity percolation from a phase transition perspective, which is the search for a spanning rigid cluster and determining its properties. The emergence of a spanning rigid cluster pinpoints the location of the transition. Therefore, its size, or number of bonds, serves as a reasonable order parameter. The dimensionality of the spanning rigid cluster at the transition location gives us information about the nature of the transition. To determine the dimensionality of the cluster, one typically measures the number of bonds in the spanning rigid cluster as a function of the system length. In two-dimensions, if the size of the spanning rigid cluster scales as L^{d_f} , where L is the system length, and $d_f = 2$, then the dimension of the rigid cluster is simply the dimension of the system and the rigid cluster is, therefore, bulky. In contrast, if $1 < d_f < 2$, then the rigid cluster is a fractal. Should the dimension of the rigid cluster be a fractal, this property points to a continuous phase transition since its size is zero in the infinite system limit at the transition but nonzero as, for example, the number of bonds are increased in the system. On the other hand, if the spanning rigid cluster is bulky at its onset, the transition is discontinuous.

Interestingly, the nature of the rigidity transition in network models of rigidity percolation can vary. For instance, the rigidity transition in the central force, randomly bond-diluted triangular lattice was numerically found to be a continuous one with $d_f = 1.86 \pm 0.02$ (Jacobs and Thorpe 1995, 1996). Meanwhile, Bethe lattices with no loops are amenable to analytical treatment and demonstrate that the spanning rigid cluster at the transition is not fractal, or bulky (Moukarzel et al. 1997; Moukarzel and Duxbury 1999; Thorpe and Stinchcombe 2014). To add to the complexity, numerical simulations of three-dimensional lattices with central-force interactions indicate a discontinuous rigidity transition as well, in contrast to the two-dimensional case (Chubynsky and Thorpe 2007). Finally, central-force models with next-neighbor springs can exhibit hybrid rigidity

transitions with both continuous and discontinuous features (Zhang et al. 2015) in terms of bulky spanning rigid cluster but having at least one diverging correlation length. This kind of hybrid transition is not unique to rigidity percolation. It has also been found in correlated percolation models inspired by jamming in which the mechanical constraints are encoded in the geometry (Harris and Schwarz 2005; Schwarz et al. 2006; Jeng and Schwarz 2007, 2010; Morone et al. 2019).

Turning now to packing problems, the contact network is a graph from which the rigid clusters can be constructed and, therefore, the spanning rigid cluster can be identified. This has been done for frictionless two-dimensional packings (derived from numerical simulations). In such packings, there is no contact graph in the fluid-like phase of the packing (zero bulk modulus), while at the transition from fluid-like to solid-like, a contact graph emerges. It turns out that every bond in the contact graph (excluding rattlers) is part of one system-spanning rigid cluster. This means that the spanning rigid cluster is bulky, or $d_f = 2$ (see Fig. 5). And while the onset of the rigid cluster is discontinuous, there is at least one diverging correlation lengths in frictionless jamming associated the divergence of the isostaticity of the packing as one begins to add

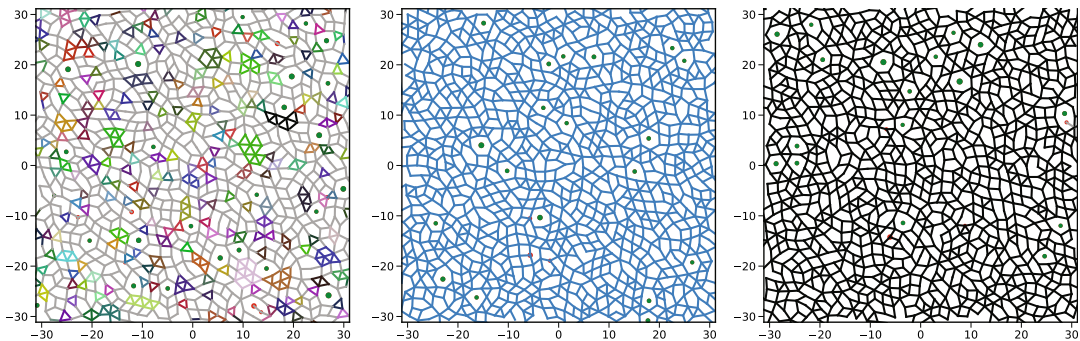
contacts further into the solid-like phase of the packing (Wyart et al. 2005). This divergence was more recently explored explicitly using rigid cluster analysis in which a smaller and smaller subsystem is carved out until there is no spanning rigid cluster (Goodrich et al. 2013).

Given that nature of the frictionless jamming transition is that of a hybrid transition, we now turn to the case with friction and ask how different is the nature of the frictional jamming transition.

The Frictional Rigidity Transition

Frictional Constraint Counting

Now that we have discussed in detail constraint counting in frictionless, or central-force, systems, let us return to frictional systems with contacts below and at the Coulomb threshold. Maxwell constraint counting for frictional packings can be generalized from Eq. 4 describing particles with both translational and rotational degrees of freedom as follows. First, at finite friction coefficient $\mu < \infty$, a number of contacts have reached the Coulomb threshold and are now sliding. Therefore, they will be unable to provide any tangential constraints on the motion, only a simple normal constraint. Let n_m be the mean number of such sliding



Rigidity Percolation and Frictional Jamming, Fig. 5 The frictionless rigidity transition on networks derived from numerically derived frictionless, two-dimensional packings just below (left) at (middle) and above (right) the frictionless jamming transition, as detailed in (Ellenbroek et al. 2006). The data for this image derives from a $\phi = 0.84$ run of the frictionless simulations in (Henkes et al. 2016). Gray bonds are floppy, and colored bonds correspond to rigid clusters. The middle

network has exactly one overconstrained bond, i.e., it is isostatic; the right network has 43 (nonunique) overconstrained bonds. Leftover pebbles are either red (one) or green (two); the isolated green dots correspond to rattlers, i.e., isolated particles not participating in the packing. There is no partial rigidity except for strictly microscopic clusters, consistent with a mean-field nature of the frictionless rigidity transition in jamming

contacts per particle. Then the total number of constraints is now only given by $N dz/2 - N(d-1)n_m$. Requiring that the number of constraints be sufficient to constrain all degrees of freedom then leads to the *generalized* isostaticity criterion (Shundyak et al. 2007; Henkes et al. 2010)

$$z^m \geq (d+1) + \frac{2(d-1)}{d} n_m - \frac{1}{N} (d+1). \quad (6)$$

In particular, in two dimensions, we recover

$$z^m \geq 3 + n_m - \frac{3}{N}. \quad (7)$$

We observe that as a function of n_m , there is now a *line* of generalized isostatic points that increases from a lower limit of $z_{iso}^\infty = 3$ when $n_m = 0$, i.e., the $\mu = \infty$ limit. For decreasing friction coefficient, we expect n_m to increase: generalized isostatic counting provides for a mechanism to explain the shifting value of z at the jamming point with μ – though empirically, the curve $z(\mu)$ obtained in simulations is monotonic, but not unique (Shundyak et al. 2007; Silbert 2010; Henkes et al. 2010) (see Fig. 6). The very carefully equilibrated simulations of (Somfai et al. 2007) are compatible with generalized isostaticity, with simulations in the zero-pressure limit falling along this line. Later analysis of the same data set using normal modes (Henkes et al. 2010) confirmed that the density of states replicates a cross-over scaling where the plateau emerges at $\omega^* \sim (z - z_{iso}^m)$, consistent with the critical scalings found in frictionless packings.

The Frictional Pebble Game

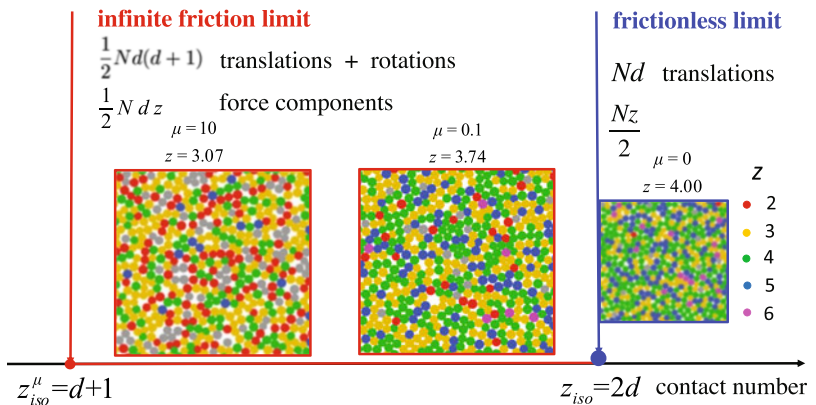
We now extend the generalization of frictionless isostaticity to Laman’s theorem and the pebble game to two-dimensional frictional packings. Consider the sample frictional packing shown in Fig. 7 (panel 1). It consists of particles that are joined by bonds which are either fully frictional (blue) or sliding (orange). We can map this packing to a graph constraint counting problem (panel 2): Every particle has three degrees of freedom (two rotations and one translation), and every frictional contact provides two constraints, while a sliding contact provides one constraint, represented by double edges and single edges, respectively. As in the frictionless case, we need to allow for three global degrees of freedom as well. While there is not currently a proof of Laman’s theorem for the frictional case, the equivalent hypothesis is:

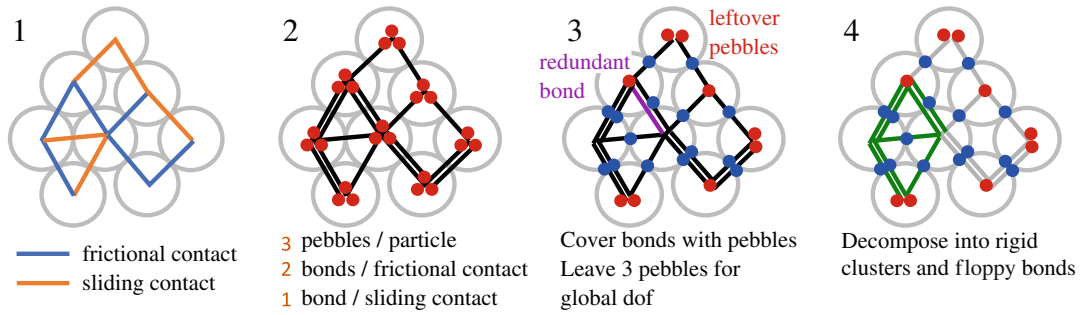
Hypothesis: *The graph G containing v vertices and e edges is infinitesimally rigid if and only if every subgraph G' , with its own v' vertices and e' edges, satisfies” $e' \leq 3v' - 3$.*

We consequently play a (3, 3) pebble game to investigate the rigidity of the graph. As shown in panel 2, we associate three pebbles to each particles. We then add the bonds representing frictional and sliding contacts to the graph one by one, using a directed search of the graph for free pebbles. As in the (2, 3) game, for every bond, we need to locate four pebbles sequentially to make sure that three global degrees of freedom remain unconstrained. In panel 3, we show the results of

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Fig. 6 Constraint counting for frictional and frictionless packings, together with representative examples of simulated packings. “Rattler” particles with less than two contacts are colored gray and are clearly visible in the $\mu = 10$ simulation. The mean contact number shown here excludes rattlers





Rigidity Percolation and Frictional Jamming, Fig. 7 The (3,3) pebble game. Step 1: A packing with frictional and sliding contacts is mapped to a graph with double and single bonds in step 2. In step 3, the three

pebbles per particle are placed on bonds where possible using the pebble game, leaving leftover pebbles and redundant bonds. In step 4, the graph is decomposed into rigid clusters (green) and floppy bonds (gray)

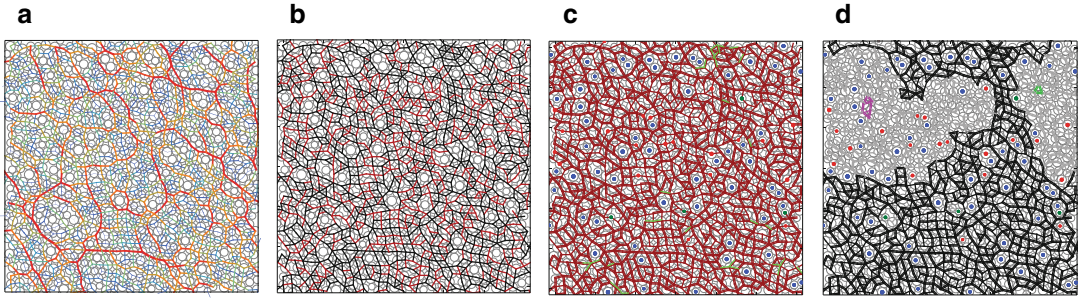
the pebble game: For most bonds, a pebble (blue) has been located and placed on the bond (black), making it part of G . For *redundant* bonds (purple), the addition process failed, signaling a local overconstraint or equivalently the existence of a (single) state of self-stress. At the same time, more than global three pebbles can remain on the graph. These leftover pebbles (red) are the unconstrained degrees of freedom. In the last stage of the process, we decompose G into rigid and floppy regions using the algorithm introduced in section “The Pebble Game.” Panel 4 shows an example of such a decomposition, with one rigid cluster (green) surrounded by floppy bonds.

Results for Lattices, Simulated, and Experimental Packings

Now that we can identify frictional rigid clusters, we summarize how frictional jamming emerges in three situations through the lens of the frictional rigidity transition: First in a simulation of soft frictional particles in simple shear Lees-Edwards boundary conditions, along the lines of section “Numerical Models” (Henkes et al. 2016); second in experimental packings of frictional disks driven by pure shear (Liu et al. 2020); and third, in a simplified frictional rigidity percolation lattice model in which the transition is tuned by controlling the number of contacts (Liu et al. 2019).

In all three cases, we apply the (3, 3) pebble game to graphs obtained from packings under different conditions. Figure 8 shows the different stages of the rigid cluster decomposition process

for a simulated packing near jamming: In panel a is the contact network, with the normal force magnitude shown as color and width; force chains oriented in the principal stress direction are clearly visible (diagonal for Lees-Edwards boundary conditions, corresponding to simple shear). Panel b shows which contacts are below the Coulomb threshold (frictional contacts, in black) and which contacts are sliding (red). This simulation was run for small friction coefficient $\mu = 0.1$, leading to a significant fraction of sliding contacts ($n_m \approx 0.55$ near jamming (Henkes et al. 2016)). In panel c, the result from the pebble game shows bonds that have been successfully added to the graph (dark red) as well as bonds that are overconstrained (green); thick lines are the double bonds corresponding to frictional contacts. Colored circles correspond to leftover pebbles on particles, with three leftover pebbles in blue (prominent on particles without contacts), but also particles with two (green) and one (red) leftover pebble. The existence of *both* overconstrained bonds and leftover pebbles on the same graph already shows that mean-field constraint counting is insufficient. Finally, panel 4 shows the decomposition of the packing into rigid subgraphs: in this particular packing, there is one large spanning rigid cluster (black), together with two other small rigid clusters (pink and green), among a sea of floppy bonds (gray). This packing is partially rigid, showing that *partial rigidity* is possible for frictional packings.



Rigidity Percolation and Frictional Jamming, Fig. 8 Decomposition of a simulated frictional packing into rigid clusters (Henkes et al. 2016). (a) Contact forces, (b) frictional (black) and sliding (red) bonds, (c) after the

pebble game, including covered bonds (red), redundant bonds (green), and leftover pebbles (three in blue, two in green, and one in red). (d) Decomposition into rigid clusters (black and colored) as well as floppy bonds (gray)

Figure 9 shows the rigid cluster decomposition for an experimental packing. The observation of a partially rigid system also emerges for the experimental system of (Liu et al. 2020). Figure 9a shows the photoelastic experimental setup. The air flow from the bottom minimizes friction with the substrate, allowing for a truly two-dimensional system. Panel b shows the photoelastic response of the packing captured through cross-polarizers; the force chains are clearly visible. Panel d shows the decomposition of this same packing into rigid clusters: as in the simulation, it is apparent that the packing is partially rigid, with two substantial rigid clusters and a smattering of small ones separated by floppy bonds.

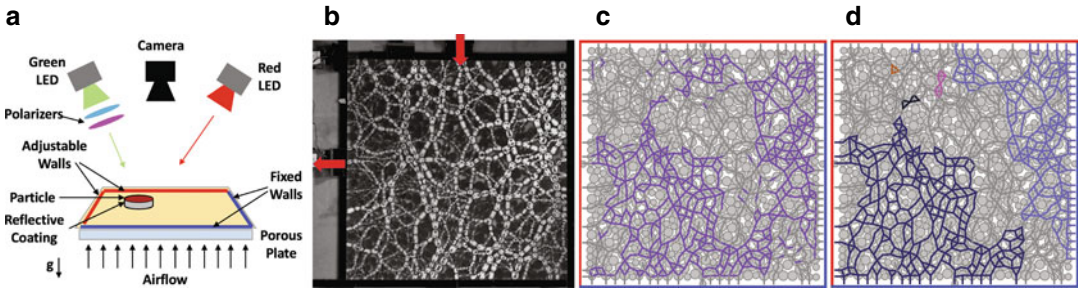
Panel c represents the results of a complementary approach to frictional rigidity. Following the Hertz-Mindlin or Cundall-Strack contact models, the incremental increase of tangential force in response to tangential sliding can be mapped to a harmonic potential for very small displacements, i.e., within the range of linear response. This effective frictional potential for contact ij in the same geometry as Fig. 2 can be written as (Somfai et al. 2007; Henkes et al. 2010; Liu et al. 2020):

$$V_{ij} = \frac{1}{2} \left[K_n (\delta \mathbf{r} \cdot \hat{\mathbf{n}})^2 = \frac{f_n}{|\mathbf{r}_{ij}|} (\delta \mathbf{r} \cdot \hat{\mathbf{t}})^2 + \delta V_{\text{eff}}^f \right], \quad (8)$$

where the last term is the effective frictional potential for an infinitesimal displacement,

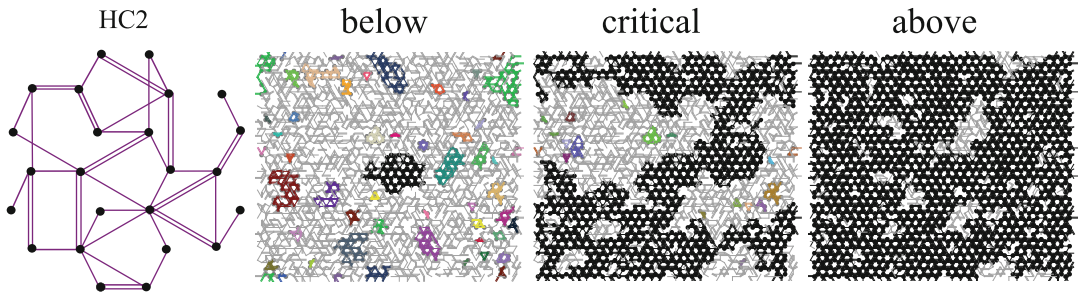
$V_{\text{eff}}^f = K_t \delta t^2$ for a frictional contact, and $V_{\text{eff}}^f = \pm \mu f_n \delta t$ for a sliding contact. As in Fig. 2 and Eq. 1, we have defined $\delta t = \delta \mathbf{r} \cdot \hat{\mathbf{t}}_{ij} - (R_i \delta \theta_i + R_j \delta \theta_j)$. Using this potential, one can define a dynamical matrix for infinitesimal translations and rotations and obtain the normal modes (eigenvectors) and their eigenvalues. A *floppy* mode corresponds to an eigenvector with zero eigenvalue, while a displacement involving constraint motions will cost energy. One can define a particle as rigid within this context if it does not participate significantly in *any* of the floppy modes in this system. Rigid regions then consist of these particles and the contacts that link them. Figure 9c shows the bonds that make up the rigid regions of the packing. It is apparent that they are strongly correlated with the rigid clusters of the pebble game, which can be quantitatively confirmed using the adjusted rand index (Liu et al. 2020).

To provide context for frictional rigidity percolation, Liu et al. (2019) created a lattice model to study the transition in detail. It consists of a honeycomb lattice with second neighbor bonds that have been randomly deleted, giving a mean contact number of $z = 3.5$, where bonds are either frictional or sliding with probability q , see Fig. 10a. As in standard percolation measures, adding bonds to the graph with probability p then either produces a percolated system or not. Figure 10 shows a schematic of the lattice model with frictional and sliding contacts together



Rigidity Percolation and Frictional Jamming, Fig. 9 Decomposition of experimental frictional packings into rigid clusters and rigid regions (Liu et al. 2020). (a) Experimental setup, (b) photoelastic response showing

forces in the packing, (c) rigid region decomposition using the dynamical matrix, and (d) decomposition into rigid clusters (colors) as well as floppy bonds (gray)



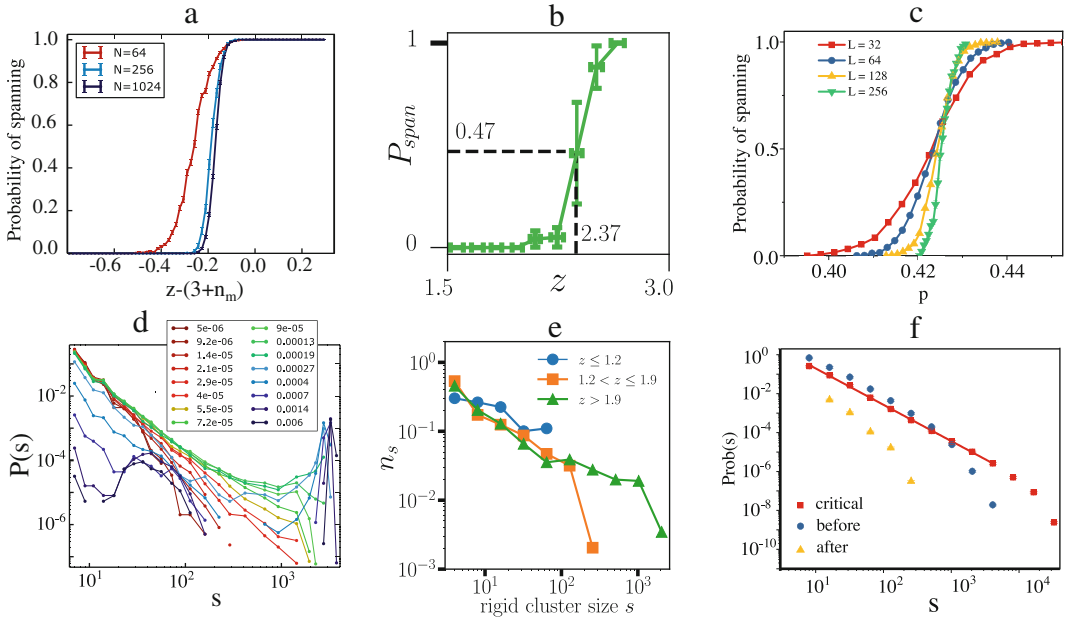
Rigidity Percolation and Frictional Jamming, Fig. 10 Rigid clusters of the (3, 3) pebble game for the lattice models of (Liu et al. 2019) as shown on the left, below, at, and above the transition

with the rigid cluster decomposition with increasing p . Here, as in the two earlier cases, one observes partial rigidity, i.e., regions of particles in contact but not part of a spanning rigid cluster, regions of particles in contact and part of a spanning rigid cluster, and a boundary between the two.

The next step for frictional rigidity percolation is to accurately determine the order of the transition and its critical exponents. Figure 11a shows the probability of a spanning rigid cluster for the numerically derived packings. The probability of spanning approaches a step function as a function of the distance to the generalized isostaticity line $dz = z - (3 + n_m)$ with growing particle number N . The transition itself is at approximately $dz = -0.2 \pm 0.05$, clearly below the mean field counting prediction $z = 3 + n_m$. Figure 11d shows the corresponding cluster size distribution, using the pressure as a proxy for distance to jamming. This distribution in the transition region $4 \times 10^{-5} < p < 2 \times 10^{-1}$ is broad on a log-log

scale, consistent with a second-order phase transition. Contrasting this result with the frictionless case, consistent with the results of Ellenbroek et al. (2006) (see Fig. 5), repeating the simulation and analysis for frictionless particles leads to a mean-field like transition (Henkes et al. 2016): there is a gap in the cluster size distribution, with packings having either a handful of very small rigid clusters or a single spanning rigid cluster. With the exception of isolated rattler particles, the spanning rigid cluster encompasses the full packing.

Figure 11b show the probability of finding a spanning rigid cluster in the experiment. The transition is again significantly below the mean-field point $z = 3$ (the fraction of sliding contacts is below 1% in the experiment), with $z_{\text{rigid}} = 2.4 \pm 0.1$. Part of the discrepancy with other experimental measures of the transition point (Majmudar and Behringer 2005; Majmudar et al. 2007) is explained by this analysis not removing rattlers, as the floppy regions are an integral part



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Fig. 11 Rigid cluster spanning probabilities (top row) and cluster size distributions (bottom row) for simulations

(Henkes et al. 2016) (left), experiment (Liu et al. 2020) (middle) and lattice model (Liu et al. 2019) (right)

of the packing. The cluster size distribution (panel e), obtained on limited statistics, is consistent with a continuous distribution, strengthening the evidence of a second order rigidity transition.

Figure 11c shows the probability of finding a spanning rigid cluster for the lattice model as a function of p and increasing system size, showing clear evidence of a phase transition for finite p . This is qualitatively consistent with the simulation (panel a) and experimental (panel b) transition curves. Panel f shows cluster size distributions below (blue) at (red) and above (yellow) the transition. There is a power law distribution in cluster size at the transition, cut off only by the system size, indicating a second order rigidity transition. Figure 10 shows examples of rigid clusters below, at and above the rigidity transition. They strongly resemble their simulated and experimental counterparts, with a sea of very small rigid clusters giving way to a rapidly appearing spanning rigid cluster that fills a substantial fraction of the system.

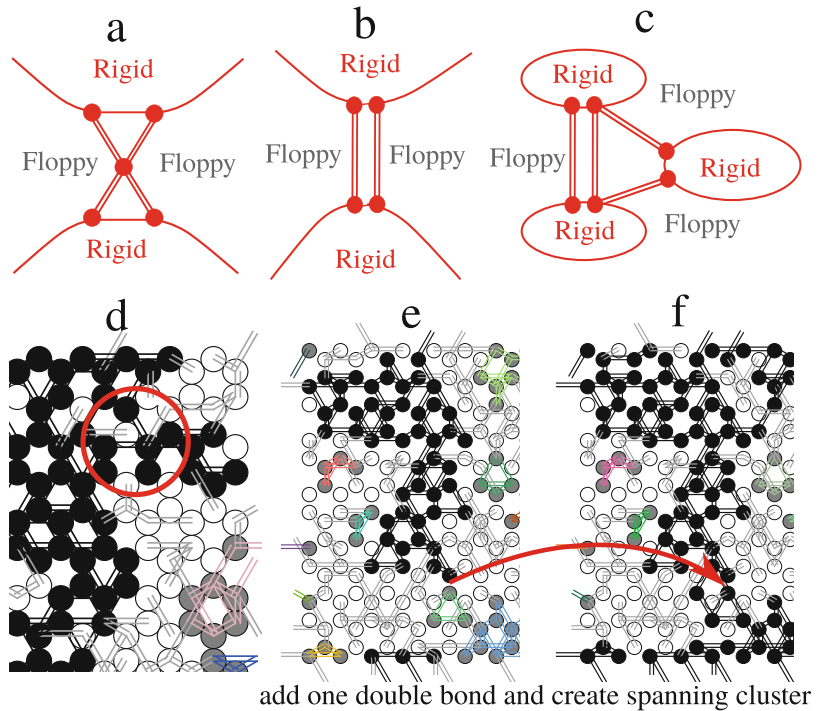
For the lattice model, careful computation of the critical exponents of the system revealed that frictional rigidity percolation (the (3, 3) game) is

in a separate universality class from standard rigidity percolation (the (2, 3) game) on the same lattice (Liu et al. 2019). The authors also extended the careful renormalization flow calculations for standard rigidity percolation on hierarchical lattices of (Thorpe and Stinchcombe 2014) to frictional rigidity percolation, again finding a separate universality class.

Consistent with the rapid appearance of the spanning rigid cluster, the fractal dimension of the spanning cluster is just below 2. Differences are apparent especially in the cluster size distribution exponent τ which falls systematically below 2. This is unusual, since standard arguments in percolation predict $\tau > 2$, which is also observed in standard rigidity percolation. The difference here is the nonadditive nature of rigid clusters (see Fig. 12): Adding only one bond can merge several disconnected rigid clusters into one giant cluster, with sets of floppy bonds suddenly becoming rigid due to the nonlocal nature of constraint counting. The narrow points of the spanning rigid cluster are dominated by several types of hinge or arch structure (panels a–c), allowing one or a pair of contacts between two particles to

Rigidity Percolation and Frictional Jamming,

Fig. 12 Mechanisms of rigid cluster mergers using hinges, from (Liu et al. 2019)



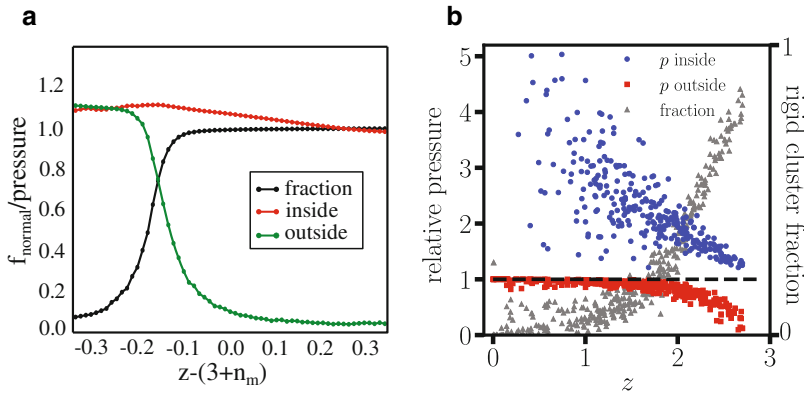
transmit rigidity. This mechanism is not possible for the (2, 3) pebble game, i.e., in frictionless rigidity percolation. It provides more options for rigid arches, and floppy holes, giving a potential explanation for why frictionless rigid clusters on graphs derived from granular packings are always space-filling (see Fig. 5).

At this point it should be said that the correspondence between rigidity and the (3, 3) pebble game is likely not exact: Lester et al. (Lester and Li 2018) tested the (3, 3) pebble game against the rank of the rigidity matrix on random planar graphs and found a subset of graphs where the two measures differ. The most prominent examples are *gearing* motions in loops of an even number of particles, where the leftover rotational degree of freedom is unrecognized by the pebble game. Since realistic packings almost always frustrate such gearing motion, the effect of such exceptions is likely limited in practice.

One is then led to ask whether or not these rigid clusters correlate with other physical properties of the packing. A measure of stress does produce a correlation between rigid clusters and high-stress regions: Fig. 13a (from the simulations of (Henkes

et al. 2016) shows the mean normal force magnitude divided by the virial pressure of a given, both inside rigid clusters (red) as well as outside rigid clusters (green). Below the transition (indicated by the black line of the fraction of the system that belongs to a rigid cluster), both regions equally support what little stress there is in the packing, indicating that rigid clusters do not play a special mechanical role; separately the pressure in these unjammed packings strongly increases with the dissipation coefficient ζ , indicating that the pressure is largely due to dissipative forces. However, as the transition is crossed, rigid clusters progressively take more of the overall load, while the forces within floppy regions sharply decreases. Well above the transition, the floppy regions morph into individual contact-less rattler particles.

In experiments (Liu et al. 2020), a very similar effect is apparent. Figure 13b shows the virial pressure inside and outside rigid clusters normalized by the packing virial pressure. Here, the pressure inside rigid clusters always exceeds the pressure in floppy regions. As in the simulation, that pressure in floppy regions is rapidly dropping as the rigidity transition is crossed. In contrast, the



Rigidity Percolation and Frictional Jamming, Fig. 13 Correlation between rigidity and pressure in simulations (left) and experiments (right). (a) Rigid cluster fraction (black) together with the normal force scaled by the pressure of a packing inside (red) and outside (green)

rigid clusters (Henkes et al. 2016). (b) Pressure scaled by the packing pressure inside (blue) and outside (red) of rigid clusters, together with the rigid fraction for experimental packings (Liu et al. 2020)

pressure in rigid clusters far exceeds the mean pressure at low contact number, potentially due to a different mechanism of dissipation in the packings under quasistatic shear steps or due to boundary effects.

Future Directions

We now have new understanding of the nature of the frictional jamming transition via rigid clusters, which correlate both with high stress regions and with rigid regions obtained from a dynamical matrix approach with an effective potential for friction. The rigid clusters have a broad range of sizes near the frictional jamming transition and are filled with regions of floppy particles despite being part of the packing. Such structures resemble those found in a continuous phase transition as is found in connectivity percolation and some models of rigidity percolation and is different from frictionless jamming and other models of correlated and rigidity percolation. How does this rigid cluster approach compare with more traditional approaches to frictional jamming? What remains unclear so far is the precise relation between frictional rigidity percolation and other aspects of frictional jamming, in particular, shear jamming. Both transitions, as measured by rigid clusters and by strong force network percolation,

respectively, occur in the same set of packings (Liu et al. 2020). There is, however, no substantial correlation between the shear jamming measure of contacts with above average force and the rigid clusters, or rigid regions, in the experiment (Liu et al. 2020). In contrast, in simulations that start from frictionless packings and then introduce normal and tangential forces compatible with friction, Vinutha et al. (Vinutha and Sastry 2016, 2019) found strong correlations between force chains and rigid clusters. This discrepancy may ultimately be resolved by exploring the differences between how the packings are generated. If indeed, there is ultimately not a strong correspondence between rigid clusters and force chains for some generically generated class of frictional packings, then one would have to tease apart the role of each characteristic and presumably their interplay. Determining the interplay between rigidity, forces, and geometry in frictional packings is a necessary ongoing task in the granular community.

There are clearly other rigidity transitions that have similarities to the onset of frictional rigidity. In addition to frictionless jamming which we have already discussed in the main text, these include shear thickening in dense suspensions and the rigidity of gels. In shear thickening, lubrication between contacts initially leads to rheology appropriate to frictionless particles in a fluid, but

as the strain rate increases, frictional contacts begin to form. Since the frictional jamming transition is at lower packing fraction, the system moves at least partially into a jammed state, leading to a sudden, enormous increase in the viscosity, the eponymous shear thickening. This transition has been investigated theoretically (Wyart and Cates 2014), numerically, and experimentally, but there is an incomplete picture of the local structure in such suspensions, and rigidity percolation techniques have so far not been applied to these systems. We expect that the different nature of the rigidity transition in frictional and frictionless systems will bear on the details of the shear thickening transition.

In gels, the jamming transition has long known to be history dependent, with strikingly different internal structures appearing depending on the strain history of the sample (Trappe et al. 2001). Recent work (Koeze and Tighe 2018; Zhang et al. 2019) has mapped out the rigid structures in these gels using the (2, 3) pebble game, finding a second order transition. This finding adds to the emerging notion that the mean field frictionless rigidity transition is the unusual case, not the second order frictional rigidity transition.

We have so far focused on particle packings. However, related questions arise within the domain of biological tissues: Epithelial cell sheets are made of living, actively driven particles that interact to produce confluent tissues with novel soft active mechanics (Nagai and Honda 2001; Farhadifar et al. 2007; Fletcher et al. 2014). Such tissues closely resemble a cobblestone pavement, with a single layer of tightly packed cells that approximate a polygonal tiling. One set of theoretical approaches describing such a tissue is known as vertex models (Nagai and Honda 2001; Farhadifar et al. 2007; Fletcher et al. 2014), where the tissue is mapped to an energy functional on the polygonal tiling. In such models, there exists a density-independent rigidity transition as a preferred shape parameter is tuned (Bi et al. 2015). One way to understand this transition is in the context of energy barriers to T1 transitions, or local cellular rearrangements. In addition, constraint counting methods have also been applied to understand how the fluidization

happens as the coordination number of the graph changes (Yan and Bi 2019). A further generalization of rigidity percolation and the pebble game to these systems will be helpful. In these same systems and more generally in spring networks, the question of rigidity at nonlinear level is also being raised: Tensegrity or rigidity through states of self-stress is important for these systems (Merkel et al. 2019), while the purely repulsive forces in the granular systems that we have considered above make those states rare at best.

Finally, this approach calls for more mathematical endeavors, such as the task of making frictional constraint counting more rigorous. While comparison with rigid regions gives us confidence in the frictional pebble game, particularly near the transition, it does not yet take into account the gear phenomenon that odd cycles/loops are frustrated, i.e., there is no gear motion. With such mathematical endeavors, we hope that the bond between the mathematicians studying rigidity theory and the physicists studying rigidity percolation will become stronger such that the origins of rigidity in systems ranging from particle packings to spring networks to vertex models will become more transparent.

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Cell Biology: Networks, Regulation and Pathways

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Glossary

Dynamical system is a set of components the properties of which (e. g. their quantity, activity level etc.) change in time because the components interact among themselves and are also influenced by external forces.

Network node is a constituent component of the network, in biological networks most often identified with a molecular species.

Interaction is a connection between network nodes; in biological networks an interaction means that two nodes chemically react, regulate each other, or effectively influence each other's activities. Interactions are mostly pairwise, but can be higher-order as well; they can be directed

or undirected, and are usually characterized by an interaction strength.

Network is a system of interacting nodes. A network can be represented mathematically as a graph, where vertices denote the nodes and edges denote the interactions. Biological networks often are understood to be dynamical systems as well, because the activities of network nodes evolve in time due to the graph of interactions.

Network state is the vector of activities of all nodes that fully characterizes the network at any point in time; since a biological network is a dynamical system, this state generally changes through time according to a set of dynamical equations.

Biological function refers to the role that a specific network plays in the life of the organism; the network can be viewed as existing to perform a task that enables the cell to survive and reproduce, such as the detection or transduction of a specific chemical signal.

Pathway is a subset of nodes and interactions in a network along which information or energy and matter flow in a directed fashion; pathways can be coupled through interactions or unwanted cross-talk.

Curse of dimensionality is the rapid increase of complexity encountered when analyzing or experimentally observing network states, as more and more network nodes are added. If there are N network nodes each of which only has two states (for example *on* and *off*), the number of states that the network can be in grows as 2^N .

Design principle is an (assumed) constraint on the network architecture, stating that a biological network, in addition to performing a certain function, implements that function in a particular way, usually to maximize or minimize some further objective measure, for instance robustness, information transmission, or designability.

Definition of the Subject

In cell biology, networks are systems of interacting molecules that implement cellular functions, such as the regulation of gene expression, metabolism or intracellular signaling. While on a molecular level a biological network is a mesh of chemical reactions between, for example, enzymes and their substrates, or DNA-binding proteins and the genes that they regulate, the collective effect of these reactions can often be thought of as the enabling and regulating the flow of matter and energy (in metabolic networks), or of information (in signaling and transcriptional regulatory networks). The field is concerned primarily with the description and properties of such flows and with their emergence from network constituent parts – the molecules and their physical interactions. An important focus is also the question of how network function and operating principles can be inferred despite the limited experimental access to network states and building blocks.

Introduction

Biological network has come to mean a system of interacting molecules that jointly perform cellular tasks such as the regulation of gene expression, information transmission, or metabolism (Bray 1995). Specific instances of biological networks include, for example, the DNA and DNA binding proteins comprising the transcriptional regulatory network; signaling proteins and small molecules comprising various signaling networks; or enzymes and metabolites comprising the metabolic network. Two important assumptions shape our current understanding of such systems: first, that the biological networks have been under selective evolutionary pressure to perform specific cellular functions in a way that furthers the overall reproductive success of the individual; and second, that these functions often are not implemented on a microscopic level by single molecules, but are rather a collective property of the whole interaction network. The question of how complex behavior emerges in a network of

(simple) nodes under a functional constraint is thus central (Strogatz 2001).

To start off with a concrete example, consider chemo-taxis in the bacterium *Escherichia coli* (Berg 1975; Falke et al. 1997), one of the paradigmatic examples of signal transduction. This system is dedicated to steering the bacteria towards areas high in nutrient substances and away from repellents. Chemo-effector molecules in the solution outside the bacterium bind to receptor molecules on the cell surface, and the resulting structural changes in the receptors are relayed in turn by the activities of the intracellular signaling proteins to generate a control signal for molecular motors that drive the bacterial flagella. The chemotactic network consists of about ten nodes (here, signaling proteins), and the interactions between the nodes are the chemical reactions of methylation or phosphorylation. Notable features of this system include its extreme sensitivity, down to the limits set by counting individual molecules as they arrive at the cell surface (Berg and Purcell 1977), and the maintenance of this sensitivity across a huge dynamic range, through an adaptation mechanism that provides nearly perfect compensation of background concentrations (Block et al. 1983). More recently it has been appreciated that aspects of this functionality, such as perfect adaptation, are also robust against large variations in the concentrations of the network components (Alon et al. 1999).

Abstractly, different kinds of signaling proteins, such those in chemotaxis, can be thought of as the building blocks of a network, with their biochemical interactions forming the wiring diagram of the system, much like the components and wiring diagram of, for instance, a radio receiver. In principle, these wiring diagrams are hugely complex; for a network composed of N species, there are $\sim C_k^N$ possible connections among any set of k components, and typically we don't have direct experimental guidance about the numbers associated with each 'wire.' One approach is to view this as giant fitting problem: once we draw a network, there is a direct translation of this graph into dynamical equations, with many parameters, and we should test the predictions of these dynamics against whatever data are

available to best determine the underlying parameters. Another approach is to ask whether this large collection of parameters is special in any way other than that it happens to fit the data – are there principles that allow us to predict how these systems *should* work? In the context of chemotaxis, we might imagine that network parameters have been selected to optimize the average progress of bacteria up the chemical gradients of nutrients, or to maximize the robustness of certain functions against extreme parameter variations. These ideas of design principles clearly are not limited to bacterial chemotaxis.

An important aspect of biological networks is that the same components (or components that have an easily identifiable evolutionary relationship) can be (re)used in different modules or used for the same function in a different way across species, as discussed for example by Rao et al. (2004) for the case of bacterial chemotaxis. Furthermore, because evolutionary selection depends on function and not directly on microscopic details, different wiring diagrams or even changes in components themselves can result in the same performance; evolutionary process can gradually change the structure of the network as long as its function is preserved; as an example see the discussion of transcriptional regulation in yeast by Tanay et al. (2005). On the other hand, one can also expect that signal processing problems like gain control, noise reduction, ensuring (bi)stability etc., have appeared and were solved repeatedly, perhaps even in similar ways across various cellular functions, and we might be able to detect the traces of their commonality in the network structure, as for example in the discussion of local connectivity in bacterial transcriptional regulation by Shen–Orr et al. (2002). Thus there are reasons to believe that in addition to design principles at the network level, there might also be local organizing principles, similar to common wiring motifs in electronic circuitry, yet still independent of the identity of the molecules that implement these principles.

Biological networks have been approached at many different levels, often by investigators from different disciplines. The basic wiring diagram of a network – the fact that a kinase phosphorylates

these particular proteins, and not all others, or that a transcription factor binds to the promoter regions of particular genes – is determined by classical biochemical and structural concepts such as binding specificity. At the opposite extreme, trying to understand the collective behavior of the network as a whole suggests approaches from statistical physics, often looking at simplified models that leave out many molecular details. Analyses that start with design principles are yet a different approach, more in the ‘top–down’ spirit of statistical physics but leaving perhaps more room for details to emerge as the analysis is refined. Eventually, all of these different views need to converge: networks really are built out of molecules, their functions emerge as collective behaviors, and these functions must really be functions of use to the organism. At the moment, however, we seldom know enough to bridge the different levels of description, so the different approaches are pursued more or less independently, and we follow this convention here. We will start with the molecular building blocks, then look at models for networks as a whole, and finally consider design principles. We hope that this sequence doesn’t leave the impression that we actually know how to build up from molecules to function!

Before exploring our subject in more detail, we take a moment to consider its boundaries. Our assignment from the editors was to focus on phenomena at the level of molecular and cellular biology. A very different approach attempts to create a ‘science of networks’ that searches for common properties in biological, social, economic and computer networks (Newman et al. 2006). Even within the biological world, there is a significant divide between work on networks in cell biology and networks in the brain. As far as we can see this division is an artifact of history, since there are many issues which cut across these different fields. Thus, some of the most beautiful work on signaling comes from photoreceptors, where the combination of optical inputs and electrical outputs allowed, already in the 1970s, for experiments with a degree of quantitative analysis that even today is hard to match in systems which take chemical inputs and give outputs that

modulate the expression levels of genes (Baylor et al. 1979; Rieke and Baylor 1998). Similarly, problems of noise in the control of gene expression have parallels in the long history of work on noise in ion channels, as we have discussed elsewhere (Tkačik et al. 2008c), and the problems of robustness have also been extensively explored in the network of interactions among the multiple species of ion channels in the membrane (Goldman et al. 2001; LeMasson et al. 1993). Finally, the ideas of collective behavior are much better developed in the context of neural networks than in cellular networks, and it is an open question how much can be learned by studying these different systems in the same language (Tkačik 2007).

Biological Networks and Their Building Blocks

Genetic Regulatory Networks

Cells constantly adjust their levels of gene expression. One central mechanism in this regulatory process involves the control of transcription by proteins known as transcription factors (TFs), which locate and bind short DNA sequences in the regulated genes' promoter or enhancer regions. A given transcription factor can regulate either a few or a sizable proportion of the genes in a genome, and a single gene may be regulated by more than one transcription factor; different transcription factors can also regulate each other (Watson et al. 2003).

In the simplest case of a gene regulated by a single TF, the gene might be expressed whenever the factor – in this case called an activator – is bound to the cognate sequence in the promoter (which corresponds to the situation when the TF concentration in the nucleus is high), whereas the binding of a repressor would shut a normally active gene down. The outlines of these basic control principles were established long ago, well before the individual transcription factors could be isolated, in elegant experiments on the *lactose* operon of *Escherichia coli* (Jacob and Monod 1961) and even simpler model systems such as phage λ (Ptashne 2004). To a great extent

the lessons learned from these experiments have provided the framework for understanding transcriptional control more generally, in prokaryotes (Ptashne 2001), eukaryotes (Kadonaga 2004), and even during the development of complex multicellular organisms (Arnosti and Kulkarni 2005).

The advent of high throughput techniques for probing gene regulation has extended our reach beyond single genes. In particular, microarrays (Brown and Botstein 1999) and the related data analysis tools, such as clustering (Eisen et al. 1998), have enabled researchers to find sets of genes, or *modules*, that are *coexpressed*, i.e. up- or down-regulated in a correlated fashion when the organism is exposed to different external conditions, and are thus probably regulated by the same set of transcription factors. Chromatin immunoprecipitation (ChIP) assays have made it possible to directly screen for short segments of DNA that known TFs bind; using microarray technology it is then possible to locate the intergenic regions which these segments belong to, and hence find the regulated genes, as has recently been done for the *Saccharomyces cerevisiae* DNA-TF interaction map (Lee et al. 2002).

These high throughput experimental approaches, combined with traditional molecular biology and complemented by sequence analysis and related mathematical tools (Siggia 2005), provide a large scale, topological view of the transcriptional regulatory network of a particular organism, where each link between two nodes (genes) in the regulatory graph implies either activation or repression (Alm and Arkin 2003). While useful for describing causal interactions and trying to predict responses to mutations and external perturbations (Levine and Davidson 2005), this picture does not explain how the network operates on a physical level: it lacks dynamics and specifies neither the strengths of the interactions nor how all the links converging onto a given node jointly exercise control over it. To address these issues, representative wild-type or simple synthetic regulatory elements and networks consisting of a few nodes have been studied extensively to construct quantitative models of the network building blocks.

For instance, combinatorial regulation of a gene by several transcription factors that bind and interact on the promoter has been considered by Buchler et al. (Buchler et al. 2003) as an example of (binary) biological computation and synthetic networks implementing such computations have been created (Guet et al. 2002; Yokobayashi et al. 2002). Building on classical work describing allosteric proteins such as hemoglobin, thermodynamic models have been used with success to account for combinatorial interactions on the operator of the λ phage (Ackers et al. 1982). More recently Bintu et al. (2005a, b) have reviewed the equilibrium statistical mechanics of such interactions, Setty et al. (2003) have experimentally and systematically mapped out the response surface of the *lac* promoter to combinations of its two regulatory inputs, cAMP and IPTG, and Kuhlman et al. (2007) have finally provided a consistent picture of the known experimental results and the thermodynamic model for the combinatorial regulation of the lactose operon. There have also been some successes in eukaryotic regulation, where Schroeder et al. (2004) used thermodynamically motivated models to detect clusters of binding sites that regulate the gap genes in morphogenesis of the fruit fly.

Gene regulation is a dynamical process composed of a number of steps, for example the binding of TF to DNA, recruitment of transcription machinery and the production of the messenger RNA, post-transcriptional regulation, splicing and transport of mRNA, translation, maturation and possible localization of proteins. While the extensive palette of such microscopic interactions represents a formidable theoretical and experimental challenge for each detailed study, on a network level it primarily induces three effects. First, each node – usually understood as the amount of gene product – in a graph of regulatory interactions is really not a single dynamical variable, but has a nontrivial internal state representing the configuration on the associated promoter, concentration of the corresponding messenger RNA etc.; the relation of these quantities to the concentration of the output protein is not necessarily straightforward, as emphasized in recent work comparing mRNA and protein levels in yeast

(Ghaemmaghami et al. 2003). Second, collapsing multiple chemical species onto a single node makes it difficult to include non-transcriptional regulation of gene expression in the same framework. Third, the response of the target gene to changes in the concentrations of its regulators will be delayed and extended in time, as in the example explored by Rosenfeld and Alon (2003).

Perhaps the clearest testimonies to the importance of dynamics in addition to network topology are provided by systems that involve regulatory loops, in which the output of a network feeds back on one of the inputs as an activator or repressor. McAdams and Shapiro (1995) have argued that the time delays in genetic regulatory elements are essential for the proper functioning of the phage λ switch, while Elowitz and Leibler (2000) have created a synthetic circuit made up of three mutually repressing genes (the “repressilator”), that exhibits spontaneous oscillations. Circadian clocks are examples of naturally occurring genetic oscillators (Young and Kay 2001).

In short, much is known about the skeleton of genetic regulatory interactions for model organisms, and physical models exist for several well studied (mostly prokaryotic) regulatory elements. While homology allows us to bridge the gap between model organisms and their relatives, it is less clear how and at which level of detail the knowledge about regulatory elements must be combined into a network to explain and predict its function.

Protein–Protein Interaction Networks

After having been produced, proteins often assemble into complexes through direct contact interactions, and these complexes are functionally active units participating in signal propagation and other pathways. Proteins also interact through less persistent encounters, as when a protein kinase meets its substrate. It is tempting to define a link in the network of protein–protein interactions by such physical associations, and this is the basis of several experimental methods which aim at a genome-wide survey of these interactions. Although starting out being relatively unreliable (with false positive rates of up to 50%), high throughput techniques like the yeast two hybrid

assay (Ito et al. 2001; Uetz et al. 2000) or mass spectrometry (Gavin et al. 2002; Ho et al. 2002) are providing data of increasing quality about protein–protein interactions, or the “interactome” (Krogan et al. 2006). While more reliable methods are being developed (Alm and Arkin 2003) and new organisms are being analyzed in this way (Giot et al. 2003; Li et al. 2004; Rual et al. 2005), the existing interaction data from high throughput experiments and curated databases has already been extensively studied.

Interpretation of the interactions in the protein network is tricky, however, due to the fact that different experimental approaches have various biases – for example, mass spectrometry is biased towards detecting interactions between proteins of high abundance, while two hybrid methods seem to be unbiased in this regard; on the other hand, all methods show some degree of bias towards different cellular localizations and evolutionary novelty of the proteins. Assessing such biases, however, currently depends not on direct calibration of the methods themselves but on comparison of the results with manually curated databases, although the databases surely have their own biases (Jansen and Gerstein 2004). It is reassuring that the intersection of various experimental results shows significantly improved agreement with the databases, but this comes at the cost of a substantial drop in coverage of the proteome (von Mering et al. 2002).

In contrast to the case of transcriptional regulation, the relationship between two interacting proteins is symmetric: if protein A binds to protein B, B also binds to A, so that the network is described by an undirected graph. Most of the studies have been focused on binary interactions that yeast two hybrid and derived approaches can probe, although spectrometry can detect multi-protein complexes as well. Estimates of number of links in these networks vary widely, even in the yeast *Saccharomyces cerevisiae*: Krogan et al. (2006) directly measure around 7100 interactions (between 2700 proteins), while Tucker et al. (2001) estimate the total to be around 13,000–17,000, and von Mering et al. (2002) would put the lower estimate at about 30,000. Apart from the experimental biases that can

influence such estimates and have been discussed already, it is important to realize that each experiment can only detect interactions between proteins that are expressed under the chosen external conditions (e. g. the nutrient medium); moreover, interactions can vary from being transient to permanent, to which various measurement methods respond differently. It will thus become increasingly important to qualify each interaction in a graph by specifying how it depends on context in which the interaction takes place.

Proteins ultimately carry out most of the cellular processes such as transcriptional regulation, signal propagation and metabolism, and these processes can be modeled by their respective network and dynamical system abstractions. In contrast, the interactome is not a dynamical system itself, but instead captures specific reactions (like protein complex assembly) and structural and/or functional relations that are present in all of the above processes. In this respect it has an important practical role of annotating currently unknown proteins through ‘guilt by association,’ by tying them into complexes and processes with a previously known function.

Metabolic Networks

Metabolic networks organize our knowledge about anabolic and catabolic reactions between the enzymes, their substrates and co-factors (such as ATP), by reducing the set of reactions to a graph representation where two substrates are joined by a link if they participate in the same reaction. For model organisms like the bacterium *Escherichia coli* the metabolic networks have been studied in depth and are publicly available (Kanehisa et al. 2002; Karp et al. 2002), and an increasing number of analyzed genomes offers sufficient sampling power to make statistical statements about the network properties across different domains of life (Jeong et al. 2000).

Several important features distinguish metabolic from protein–protein interaction and transcriptional regulation networks. First, for well studied systems the coverage of metabolic reactions is high, at least for the central routes of energy metabolism and small molecule synthesis; notice that this is a property of our knowledge, not

a property of the networks (!). Second, cellular concentrations of metabolites usually are much higher than those of transcription factors, making the stochasticity in reactions due to small molecular counts irrelevant. Third, knowledge of the stoichiometry of reactions allows one to directly write down a system of first order differential equations for the metabolite fluxes (Heinrich and Schuster 1996), which in steady state reduces to a set of linear constraints on the space of solutions. These chemical constraints go beyond topology and can yield strong and testable predictions; for example, Ibarra et al. (2002) have shown how computationally maximizing the growth rate of *Escherichia coli* within the space of allowed solutions given by flux balance constraints can correctly predict measurable relationships between oxygen and substrate uptake, and that bacteria can be evolved towards the predicted optimality for growth conditions in which the response was initially suboptimal.

Signaling Networks

Signaling networks consist of receptor and signaling proteins that integrate, transmit and route information by means of chemical transformations of the network constituents. One class of such transformations, for example, are post-translational modifications, where targets are phosphorylated, methylated, acetylated, ... on specific residues, with a resulting change in their enzymatic (and thus signaling) activity. Alternatively, proteins might form stable complexes or dissociate from them, again introducing states of differential activity. The ability of cells to modify or tag proteins (possibly on several residues) can increase considerably the cell's capacity to encode its state and transmit information, assuming that the signaling proteins are highly specific not only for the identity but also the modification state of their targets; for a review see Papin et al. (2005).

Despite the seeming overlap between the domains of protein-protein network and signaling networks, the focus of the analysis is substantially different. The inter-actome is simply a set of possible protein-protein interactions and thus a topological (or connectivity) map; in contrast, signaling networks aim to capture signal

transduction and therefore need to establish a causal map, in which the nature of the protein-protein interaction, its direction and timescale, and its quantitative effect on the activity of the target protein matter. As an example, see the discussion by Kolch (2000) on the role of protein-protein interactions in MAPK signaling cascade.

Experiments on some signaling systems, such as the *Escherichia coli* chemotactic module, have generated enough experimental data to require detailed models in the form of dynamical equations. Molecular processes in a signaling cascade extend over different time scales, from milliseconds required for kinase and phosphatase reactions and protein conformational changes, to minutes or more required for gene expression control, cell movement and receptor trafficking; this fact, along with the (often essential) spatial effects such as the localization of signaling machinery and diffusion of chemical messengers, can considerably complicate analyses and simulations.

Signaling networks are often factored into pathways that have specific inputs, such as the ligands of the G protein coupled receptors on the cell surface, and specific outputs, as with pathways that couple to the transcriptional regulation apparatus or to changes in the intracellular concentration of messengers such as calcium or cyclic nucleotides. Nodes in signaling networks can participate in several pathways simultaneously, thus enabling signal integration or potentially inducing damaging "crosstalk" between pathways; how junctions and nodes process signals is an area of active research (Jordan et al. 2000).

The components of signaling networks have long been the focus of biochemical research, and genetic methods allow experiments to assess the impact of knocking out or over-expressing particular components. In addition, several experimental approaches are being designed specifically for elucidating signaling networks. Ab-chips localize various signaling proteins on chips reminiscent of DNA microarrays, and stain them with appropriate fluorescent antibodies (Nielsen et al. 2003). Multicolor flow cytometry is performed on cells immuno-stained for signaling protein modifications and hundreds of single cell simultaneous

measurements of the modification state of pathway nodes are collected (Perez and Nolan 2002). Indirect inference of signaling pathways is also possible from genomic or proteomic data.

One well studied signal transduction system is the mitogen activated protein kinase (MAPK) cascade that controls, among other functions, cell proliferation and differentiation (Chang and Karin 2001). Because this system is present in all eukaryotes and its structural components are used in multiple pathways, it has been chosen as a paradigm for the study of specificity and crosstalk. Similarly, the TOR system, identified initially in yeast, is responsible for integrating the information on nutrient availability, growth factors and energy status of the cell and correspondingly regulating the cell growth (Martin and Hall 2005). Another interesting example of signal integration and both intra- and inter-cellular communication is observed in the quorum sensing circuit of the bacterium *Vibrio harveyi*, where different kinds of species- and genus-specific signaling molecules are detected by their cognate receptors on the cell surface, and the information is fed into a common *Lux* phosphorelay pathway which ultimately regulates the quorum sensing genes (Waters and Bassler 2005).

Models of Biological Networks

Topological Models

The structural features of a network are captured by its connectivity graph, where interactions (reactions, structural relations) are depicted as the links between the interacting nodes (genes, proteins, metabolites). Information about connectivity clearly cannot and does not describe the network behavior, but it might influence and constrain it in revealing ways, similar to effect that the topology of the lattice has on the statistical mechanics of systems living on it.

Theorists have studied extensively the properties of regular networks and random graphs starting with Erdős and Rényi in 1960s. The first ones are characterized by high symmetry inherent in a square, triangular, or all-to-all (mean field) lattice; the random graphs were without such

regularity, constructed simply by distributing K links at random between N nodes. The simple one-point statistical characterization that distinguishes random from regular networks looks at the node degree, that is the probability $P(k)$ that any node has k incoming and/or outgoing links. For random graphs this distribution is Poisson, meaning that most of the nodes have degrees very close to the mean, $\langle k \rangle = \sum_k k P(k)$, although there are fluctuations; for regular lattices every node has the same connectivity to its neighbors.

The first analyses of the early reconstructions of large metabolic networks revealed a surprising “scale free” node degree distribution, that is $P(k) \sim k^{-\gamma}$, with γ between two and three for most networks. For the physics community, which had seen the impact of such scale invariance on our understanding of phase transitions, these observations were extremely suggestive. It should be emphasized that for many problems in areas as diverse as quantum field theory, statistical mechanics and dynamical systems, such scaling relations are much more than curiosities. Power laws relating various experimentally observable quantities are exact (at least in some limit), and the exponents (here, γ) really contain everything one might want to know about the nature of order in the system. Further, some of the first thoughts on scaling emerged from phenomenological analyses of real data. Thus, the large body of work on scaling ideas in theoretical physics set the stage for people to be excited by the experimental observation of power laws in much more complex systems, although it is not clear to us whether the implied promise of connection to a deeper theoretical structure has been fulfilled. For divergent views on these matters see Barabási (2002) and Keller (2005).

The most immediate practical consequence of a scale free degree distribution is that – relative to expectations based on random graphs – there will be an over-representation of nodes with very large numbers of links, as with pyruvate or co-enzyme A in metabolic networks (Jeong et al. 2000; Wagner and Fell 2001). These are sometimes called hubs, although another consequence of a scale free distribution is that there is no ‘critical degree of connection’ that distinguishes hubs from non-

hubs. In the protein–protein interaction network of *Saccharomyces cerevisiae*, nodes with higher degree are more likely to represent essential proteins (Jeong et al. 2001), suggesting that node degree does have some biological meaning. On the theoretical side, removal of a sizable fraction of nodes from a scale free network will neither increase the network diameter much, nor partition the network into equally sized parts (Albert et al. 2000), and it is tempting to think that this robustness is also biologically significant. The scale free property has been observed in many non-biological contexts, such as the topology of social interactions, World Wide Web links, electrical power grid connectivity ... (Strogatz 2001). A number of models have been proposed for how such scaling might arise, and some of these ideas, such as growth by preferential attachment, have a vaguely biological flavor (Barabasi and Albert 1999; Barabasi and Oltvai 2004). Finding the properties of networks that actually discriminate among different mechanisms of evolution or growth turns out to be surprisingly subtle (Ziv et al. 2005a).

Two other revealing measures are regularly computed for biological networks. The mean path length, $\langle l \rangle$, is the shortest path between a pair of nodes, averaged over all pairs in the graph, and measures the network's overall 'navigability.' Intuitively, short path lengths correspond to, for example, efficient or fast flow of information and energy in signaling or metabolic networks, quick spread of diseases in a social network and so on. The clustering coefficient of a node i is defined as $C_i = 2n_i/k_i(k_i - 1)$, where n_i is the number of links connecting the k_i neighbors of node i to each other; equivalently, C_i is the ratio between the number of triangles passing through two neighbors of i and node i itself, divided by the maximum possible number of such triangles. Random networks have low path lengths and low clustering coefficients, whereas regular lattices have long path lengths and are locally clustered. Watts and Strogatz (1998) have constructed an intermediate regime of "small world" networks, where the regular lattice has been perturbed by a small number of random links connecting distant parts of the network together.

These networks, although not necessarily scale free, have short path lengths and high clustering coefficients, a property that was subsequently observed in metabolic and other biological networks as well (Wagner and Fell 2001).

A high clustering coefficient suggests the existence of densely connected groups of nodes within a network, which seems contradictory to the idea of scale invariance, in which there is no inherent group or cluster size; Ravasz et al. (2002) addressed this problem by introducing hierarchical networks and providing a simple construction for synthetic hierarchical networks exhibiting both scale free and clustering behaviors. Although there is no unique scale for the clusters, clusters will appear at any scale one chooses to look at, and this is revealed by the scaling of clustering coefficient $C(k)$ with the node degree k , $C(k) \sim k^{-1}$, on both synthetic as well as natural metabolic networks of organisms from different domains of life (Ravasz et al. 2002). Another interesting property of some biological networks is an anti-correlation of node degree of connected nodes (Maslov and Sneppen 2002), which we can think of as a 'dissociative' structure; in contrast, for example, with the associative character of social networks, where well connected people usually know one another.

As we look more finely at the structure of the graph representing a network, there is of course a much greater variety of things to look at. For example, Spirin and Mirny (2003) have focused on high clustering coefficients as a starting point and devised algorithms to search for modules, or densely connected subgraphs within the yeast protein–protein interaction network. Although the problem has combinatorial complexity in general, the authors found about 50 modules (of 5–10 proteins in size, some of which were unknown at the time) that come in two types: the first represents dynamic functional units (e. g. signaling cascades), and the second protein complexes. A similar conclusion was reached by Han et al. (2004), after having analyzed the interactome in combination with the temporal gene expression profiles and protein localization data; the authors argue that nodes of high degree can sit either at the centers of modules, which are simultaneously

expressed (“party hubs”), or they can be involved in various pathways and modules at different times (“date hubs”). The former kind is at a lower level of organization, whereas the latter tie the network into one large connected component.

Focusing on even a smaller scale, Shen-Orr et al. (2002) have explored motifs, or patterns of connectivity of small sets of nodes that are over-represented in a given network compared to the randomized networks of the same degree distribution $P(k)$. In the transcriptional network of the bacterium *E. coli*, three such motifs were found: feed forward loops (in which gene X regulates Y that regulates Z, but X directly regulates Z as well), single input modules (where gene X regulates a large number of other genes in the same way and usually auto-regulates itself), and dense overlapping regulons (layers of overlapping interactions between genes and a group of transcription factors, much denser than in randomized networks). The motif approach has been extended to combined network of transcriptional regulation and protein–protein interactions (Yeager-Lotem et al. 2004) in yeast, as well as to other systems (Milo et al. 2004).

At the risk of being overly pessimistic, we should conclude this section with a note of caution. It would be attractive to think that a decade of work on network topology has resulted in a coherent picture, perhaps of the following form: on the smallest scale, the nodes of biological networks are assembled into motifs, these in turn are linked into modules, and this continues in a hierarchical fashion until the entire network is scale free. As we will discuss again in the context of design principles, the notion of such discrete substructure – motifs and modules – is intuitively appealing, and some discussions suggest that it is essential either for the function or the evolution of networks. On the other hand, the evidence for such structure usually is gathered with reference to some null model (e. g., a random network with the same $P(k)$), so we don’t even have an absolute definition of these structures, much less a measure of their sufficiency as a characterization of the whole system; for attempts at an absolute definition of modularity see Ziv et al. (2005b) and Hofman and Wiggins (2007). Similarly, while it

is appealing to think about scale free networks, the evidence for scaling almost always is confined to less than two decades, and in practice scaling often is not exact. It is then not clear whether the idealization of scale invariance captures the essential structure in these systems.

Boolean Networks

A straightforward extension of the topological picture that also permits the study of network dynamics assumes that the entities at the nodes – for example, genes or signaling proteins – are either ‘on’ or ‘off’ at each moment of time, so that for node i the state at time t is $\sigma_i(t) \in \{0, 1\}$. Time is usually discretized, and an additional prescription is needed to implement the evolution of the system: $\sigma_i(t + 1) = f_i(\{\sigma_\mu(t)\})$, where f_i is a function that specifies how the states of the nodes μ that are the inputs to node i in the interaction graph combine to determine the next state at node i . For instance, f_A might be a Boolean function for gene A , which needs to have its activator gene B present and repressor gene C absent, so that $\sigma_A(t + 1) = \sigma_B(t) \wedge \bar{\sigma}_C(t)$. Alternatively, f might be a function that sums the inputs at state t with some weights, and then sets $\sigma_i = 1(0)$ if the result is above (below) a threshold, as in classical models of neural networks.

Boolean networks are amenable both to analytical treatment and to efficient simulation. Early on, Kauffman (1969) considered the family of random boolean networks. In these models, each node is connected at random to K other nodes on average, and it computes a random Boolean function of its inputs in which a fraction ρ of the 2^K possible input combinations leads to $\sigma_i(t + 1) = 1$. In the limit that the network is large, the dynamics are either regular (settling into a stable fixed cycle) or chaotic, and these two phases are separated by a separatrix $2\rho(1 - \rho)K = 1$ in the phase space (ρ, K) .

Aldana and Cluzel (2003) have shown that for connectivities of $K \sim 20$ that could reasonably be expected in e.g. transcriptional regulatory networks, the chaotic regime dominates the phase space. They point out, however, that if the network is scale free, there is no ‘typical’ K as the distribution $P(k) \sim k^{-\gamma}$ does not have a well-defined mean for $\gamma \leq 3$ and the phase transition

criterion must be restated. It turns out, surprisingly, that regular behavior is possible for values of γ between 2 and 2.5, observed in most biological networks, and this is exactly the region where the separatrix lies. Scale free architecture, at least for Boolean networks, seems to prevent chaos.

Several groups have used Boolean models to look at specific biological systems. Thomas (Thomas 1973) has established a theoretical framework in which current states of the genes (as well as the states in the immediate past) and the environmental inputs are represented by Boolean variables that evolve through the application of Boolean functions. This work has been continued by, for example, Sanchez and Thieffry (2001) who analyzed the gap-gene system of the fruit fly *Drosophila* by building a Boolean network that generates the correct levels of gene expression for 4 gap genes in response to input levels of 3 maternal morphogens with spatially varying profiles stretched along the anterior-posterior axis of the fly embryo. Interestingly, to reproduce the observed results and correctly predict the known *Drosophila* segmentation mutants, the authors had to introduce generalized Boolean variables that can take more than two states, and have identified the smallest necessary number of such states for each gene.

In a similar spirit, Li et al. (2004) studied the skeleton of the budding yeast cell cycle, composed of 11 nodes, and a thresholding update rule. They found that the topology of this small network generates a robust sequence of transitions corresponding to known progression through yeast cell-cycle phases G1 (growth), S (DNA duplication), G2 (pause) and M (division), triggered by a known ‘cell-size checkpoint.’ This progression is robust, in the sense that the correct trajectory is the biggest dynamical attractor of the system, with respect to various choices of update rules and parameters, small changes in network topology, and choice of triggering checkpoints.

The usefulness of Boolean networks stems from the relative ease of implementation and simple parametrization of network topology and dynamics, making them suitable for studying medium or large networks. In addition to simplifying the states at the nodes to two (or more) discrete levels, which is an assumption that has

not been clearly explored, one should be cautious that the discrete and usually synchronous dynamics in time can induce unwanted artifacts.

Probabilistic Models

Suppose one is able to observe simultaneously the activity levels of several proteins comprising a signaling network, or the expression levels of a set of genes belonging to the same regulatory module. Because they are part of a functional whole, the activity levels of the components will be correlated. Naively, one could build a network model by simply computing pairwise correlation coefficients between pairs of nodes, and postulating an interaction, and therefore a link, between the two nodes whenever their correlation is above some threshold. However, in a test case where $A \rightarrow B \rightarrow C$ (gene A induces B which induces C), one expects to see high positive correlation among all three elements, even though there is no (physical) interaction between A and C. Correlation therefore is not equal to interaction or causation. Constructing a network from the correlations in this naive way also does not lead to a generative model that would predict the probabilities for observing different states of the network as a whole. Another approach is clearly needed; see Markowitz and Spang (2007) for a review.

In the simple case where the activity of a protein/gene i can either be ‘on’ ($\sigma_i = 1$) or ‘off’ ($\sigma_i = 0$), the state of a network with N nodes will be characterized by a binary word of N bits, and because of interaction between nodes, not all these words will be equally likely. For example, if node A represses node B, then combinations such as $1_A 0_B \dots$ or $0_A 1_B \dots$ will be more likely than $1_A 1_B \dots$. In the case of deterministic Boolean networks, having node A be ‘on’ would imply that node B is ‘off’ with certainty, but in probabilistic models it only means that there is a positive *bias* for node B to be ‘off,’ quantified by the probability that node B is ‘off’ given that the state of node A is known. Having this additional probabilistic degree of freedom is advantageous, both because the network itself might be noisy, and because the experiment can induce errors in the signal readout, making the inference of deterministic rules from observed binary patterns an ill-posed problem.

Once we agree to make a probabilistic model, the goal is to find the distribution over all network states, which we can also think of as the joint distribution of all the N variable that live on the nodes of the network, $P(\sigma_1, \dots, \sigma_N | C)$, perhaps conditioned on some fixed set of environmental or experimental factors C . The activities of the nodes, σ_i , can be binary, can take on a discrete set of states, or be continuous, depending on our prior knowledge about the system and experimental and numerical constraints. Even for a modest N , experiments of realistic scale will not be enough to directly estimate the probability distribution, since even with binary variable the number of possible states, and hence the number of parameters required to specify the general probability distribution, grows as $\sim 2^N$. Progress thus depends in an essential way on simplifying assumptions.

Returning to the three gene example $A \rightarrow B \rightarrow C$, we realize that C depends on A only through B , or in other words, C is *conditionally independent* of A and hence no interaction should be assigned between nodes A and C . Thus, the joint distribution of three variables can be factorized,

$$P(\sigma_A, \sigma_B, \sigma_C) = P(\sigma_C | \sigma_B) P(\sigma_B | \sigma_A) P(\sigma_A).$$

One might hope that, even in a large network, these sorts of conditional independence relations could be used to simplify our model of the probability distribution. In general this doesn't work, because of feedback loops which, in our simple example, would include the possibility that C affects the state of A , either directly or through some more circuitous path. Nonetheless one can try to make an approximation in which loops either are neglected or (more sensibly) taken into account in some sort of average way; in statistical mechanics, this approximation goes back at least to the work of Bethe (1935).

In the computer science and bioinformatics literature, the exploitation of Bethe-like approximations has come to be known as 'Bayesian network modeling' (Gardner et al. 2000). In practice what this approach does is to search among possible network topologies, excluding loops, and

then for fixed topology one uses the conditional probability relationships to factorize the probability distribution and fit the tables of conditional probabilities at each node that will best reproduce some set of data. Networks with more links have more parameters, so one must introduce a trade-off between the quality of the fit to the data and this increasing complexity. In this framework there is thus an explicit simplification based on conditional independence, and an implicit simplification based on a preference for models with fewer links or sparse connectivity.

The best known application of this approach to a biological network is the analysis of the MAPK signaling pathway in T cells from the human immune system (Sachs et al. 2005). The data for this analysis comes from experiments in which the phosphorylated states of 11 proteins in the pathway are sampled simultaneously by immunostaining (Perez and Nolan 2002), with hundreds of cells sampled for each set of external conditions. By combining experiments from multiple conditions, the Bayesian network analysis was able to find a network of interactions among the 11 proteins that has high overlap with those known to occur experimentally.

A very different approach to simplification of probabilistic models is based on the maximum entropy principle (Jaynes 1957). In this approach one views a set of experiments as providing an estimate of some set of correlations, for example the $\sim N^2$ correlations among all pairs of elements in the network. One then tries to construct a probability distribution which matches these correlations but otherwise has as little structure – as much entropy – as possible. We recall that the Boltzmann distribution for systems in thermal equilibrium can be derived as the distribution which has maximum entropy consistent with a given average energy, and maximum entropy modeling generalizes this to take account of other average properties. In fact one can construct a hierarchy of maximum entropy distributions which are consistent with higher and higher orders of correlation (Schneidman et al. 2003). Maximum entropy models for binary variables that are consistent with pairwise correlations are exactly the Ising models of statistical physics,

which opens a wealth of analytic tools and intuition about collective behavior in these systems.

In the context of biological networks (broadly construed), recent work has shown that maximum entropy models consistent with pairwise correlations are surprisingly successful at describing the patterns of activity among populations of neurons in the vertebrate retina as it responds to natural movies (Schneidman et al. 2006; Tkačik et al. 2006). Similar results are obtained for very different retinas under different conditions (Shlens et al. 2006), and these successes have touched a flurry of interest in the analysis of neural populations more generally. The connection to the Ising model has a special resonance in the context of neural networks, where the collective behavior of the Ising model has been used for some time as a prototype for thinking about the dynamics of computation and memory storage (Hopfield 1982); in the maximum entropy approach the Ising model emerges directly as the least structured model consistent with the experimentally measured patterns of correlation among pairs of cells. A particularly striking result of this analysis is that the Ising models which emerge seem to be poised near a critical point (Tkačik et al. 2006). Returning to cell biology, the maximum entropy approach has also been used to analyze patterns of gene expression in yeast (Lezon et al. 2006) as well as to revisit the MAPK cascade (Tkačik 2007).

Dynamical Systems

If the information about a biological system is detailed enough to encompass all relevant interacting molecules along with the associated reactions and estimated reaction rates, and the molecular noise is expected to play a negligible role, it is possible to describe the system with rate equations of chemical kinetics. An obvious benefit is the immediate availability of mathematical tools, such as steady state and stability analyses, insight provided by nonlinear dynamics and chaos theory, well developed numerical algorithms for integration in time and convenient visualization with phase portraits or bifurcation diagrams. Moreover, analytical approximations can be often exploited productively when warranted by

some prior knowledge, for example, in separately treating ‘fast’ and ‘slow’ reactions. In practice, however, reaction rates and other important parameters are often unknown or known only up to order-of-magnitude estimations; in this case the problem usually reduces to the identification of phase space regions where the behavior of the system is qualitatively the same, for example, regions where the system exhibits limit-cycle oscillations, bistability, convergence into a single steady state etc.; see Tyson et al. (2001) for a review. Despite the difficulties, deterministic chemical kinetic models have been very powerful tools in analyzing specific network motifs or regulatory elements, as in the protein signaling circuits that achieve perfect adaptation, homeostasis, switching and so on, described by Tyson et al. (2003), and more generally in the analysis of transcriptional regulatory networks as reviewed by Hasty et al. (2001).

In the world of bacteria, some of the first detailed computer simulations of the chemotaxis module of *Escherichia coli* were undertaken by Bray et al. (1993). The signaling cascade from the Tar receptor at the cell surface to the modifications in the phosphorylation state of the molecular motor were captured by Michaelis–Menten kinetic reactions (and equilibrium binding conditions for the receptor), and the system of equations was numerically integrated in time. While slow adaptation kinetics was not studied in this first effort, the model nevertheless qualitatively reproduces about 80 percent of examined chemotactic protein deletion and overexpression mutants, although the extreme sensitivity of the system remained unexplained.

In eukaryotes, Novak and Tyson (1997) have, for instance, constructed an extensive model of cell cycle control in fission yeast. Despite its complexity (~10 proteins and ~30 rate constants), Novak and colleagues have provided an interpretation of the system in terms of three interlocking modules that regulate the transitions from G1 (growth) into S (DNA synthesis) phase, from G2 into M (division) phase, and the exit from mitosis, respectively. The modules are coupled through cdc2/cdc13 protein complex and the system is driven by the interaction with the cell size signal

(proportional to the number of ribosomes per nucleus). At small size, the control circuit can only support one stable attractor, which is the state with low *cdc2* activity corresponding to G1 phase. As the cell grows, new stable state appears and the system makes an irreversible transition into S/G2 at a bifurcation point, and, at an even larger size, the mitotic module becomes unstable and executes limit cycles in *cdc2-cdc13* activity until the M phase is completed and the cell returns to its initial size. The basic idea is that the cell, driven by the size readout, progresses through robust cell states created by bistability in the three modules comprising the cell cycle control – in this way, once it commits to a transition from G2 state into M, small fluctuations will not flip it back into G2. The mathematical model has in this case successfully predicted the behaviors of a number of cell cycle mutants and recapitulated experimental observations collected during 1970s and 1980s by Nurse and collaborators (Nurse 2001).

The circadian clock is a naturally occurring transcriptional module that is particularly amenable to dynamical systems modeling. Leloup and Goldbeter (2003) have created a mathematical model of a mammalian clock (with ~20 rate equations) that exhibits autonomous sustained oscillations over a sizable range of parameter values, and reproduces the entrainment of the oscillations to the light–dark cycles through light-induced gene expression. The basic mechanism that enables the cyclic behavior is negative feedback transcriptional control, although the actual circuit contains at least two coupled oscillators. Studying circadian clock in mammals, the fruit fly *Drosophila* or *Neurospora* is attractive because of the possibility of connecting a sizable catalogue of physiological disorders in circadian rhythms to malfunctions in the clock circuit and direct experimentation with light-dark stimuli (Young and Kay 2001). Recent experiments indicate that at least in cyanobacteria the circadian clock can be reconstituted from a surprisingly small set of biochemical reactions, without transcription or translation (Nakajima et al. 2005; Tomita et al. 2005), and this opens possibilities for even simpler and highly predictive dynamical models (Rust et al. 2007).

Dynamical modeling has in addition been applied to many smaller systems. For example, the construction of a synthetic toggle switch (Gardner et al. 2000), and the ‘repressilator’ – oscillating network of three mutually repressing genes (Elowitz and Leibler 2000) – are examples where mathematical analysis has stimulated the design of synthetic circuits. A successful reaction-diffusion model of how localization and complex formation of Min proteins can lead to spatial limit cycle oscillations (used by *Escherichia coli* to find its division site) was constructed by Huang et al. (2003). It remains a challenge, nevertheless, to navigate in the space of parameters as it becomes ever larger for bigger networks, to correctly account for localization and count various forms of protein modifications, especially when the signaling networks also couple to transcriptional regulation, and to find a proper balance between models that capture all known reactions and interactions and phenomenological models that include coarse-grained variables.

Stochastic Dynamics

Stochastic dynamics is in principle the most detailed level of system description. Here, the (integer) count of every molecular species is tracked and reactions are drawn at random with appropriate probabilities per unit time (proportional to their respective reaction rates) and executed to update the current tally of molecular counts. An algorithm implementing this prescription, called the stochastic simulation algorithm or SSA, was devised by Gillespie (1977); see Gillespie (2007) for a review of SSA and a discussion of related methods. Although slow, this approach for simulating chemical reactions can be made exact. In general, when all molecules are present in large numbers and continuous, well-mixed concentrations are good approximations, the (deterministic) rate dynamics equations and stochastic simulation give the same results; however, when molecular counts are low and, consequently, the stochasticity in reaction timing and ordering becomes important, the rate dynamics breaks down and SSA needs to be used. In biological networks and specifically in transcriptional regulation, a gene and its promoter region are only present in one (or perhaps a few) copies, while

transcription factors that regulate it can also be at nanomolar concentrations (i. e. from a few to a few hundred molecules per nucleus), making stochastic effects possibly very important (McAdams and Arkin 1997, 1999).

One of the pioneering studies of the role of noise in a biological system was a simulation of the phage λ lysis-lysogeny switch by Arkin et al. (1998). The life cycle of the phage is determined by the concentrations of two transcription factors, *cI* (lambda repressor) and *cro*, that compete for binding to the same operator on the DNA. If *cI* is prevalent, the phage DNA is integrated into the host's genome and no phage genes except for *cI* are expressed (the lysogenic state); if *cro* is dominant, the phage is in lytic state, using cell's DNA replication machinery to produce more phages and ultimately lyse the host cell (Ptashne 2004). The switch is bistable and the fate of the phage depends on the temporal and random pattern of gene expression of two mutually antagonistic transcription factors, although the balance can be shifted by subjecting the host cell to stress and thus flipping the toggle into lytic phase. The stochastic simulation correctly reproduces the experimentally observed fraction of lysogenic phages as a function of multiplicity-of-infection. An extension of SSA to spatially extended models is possible.

Although the simulations are exact, they are computationally intensive and do not offer any analytical insight into the behavior of the solutions. As a result, various theoretical techniques have been developed for studying the effects of stochasticity in biological networks. These are often operating in a regime where the deterministic chemical kinetics is a good approximation, and noise (i. e. fluctuation of concentrations around the mean) is added into the system of differential equations as a perturbation; these Langevin methods have been useful for the study of noise propagation in regulatory networks (van Kampen 2007; Paulsson 2004; Thattai and van Oudenaarden 2001). The analysis of stochastic dynamics is especially interesting in the context of design principles which consider the reliability of network function, to which we return below.

Network Properties and Operating Principles

Modularity

Biological networks are said to be modular, although the term has several related but nevertheless distinct meanings. Their common denominator is the idea that there exist a partitioning of the network nodes into groups, or modules, that are largely independent of each other and perform separate or autonomous functions. Independence can be achieved through spatial isolation of the module's processes or by chemical specificity of its components. The ability to extract the module from the cell and reconstitute it in vitro, or transplant it to another type of cell is a powerful argument for the existence of modularity (Hartwell et al. 1999). In the absence of such strong and laborious experimental verifications, however, measures of modularity that depend on a particular network model are frequently used.

In topological networks, the focus is on the module's independence: nodes within a module are densely connected to each other, while inter-modular links are sparse (Han et al. 2004; Ravasz et al. 2002; Spirin and Mirny 2003) and the tendency to cluster is measured by high clustering coefficients. As a caveat to this view note that despite their sparseness the inter-module links could represent strong dynamical couplings. Modular architecture has been studied in Boolean networks by Kashtan and Alon (2005), who have shown that modularity can evolve by mutation and selection in a time-varying fitness landscape where changeable goals decompose into a set of fixed subproblems. In the example studied they computationally evolve networks implementing several Boolean formulae and observe the appearance of a module – a circuit of logical gates implementing a particular Boolean operator (like XOR) in a reusable way. This work makes clear that modularity in networks is plausibly connected to modularity in the kinds of problems that these networks were selected to solve, but we really know relatively little about the formal structure of these problems.

There are also ways of inferring a form of modularity directly without assuming any

particular network model. Clustering tools partition genes into co-expressed groups, or clusters, that are often identified with particular modules (Eisen et al. 1998; Segal et al. 2003; Slonim et al. 2005). Ihmels et al. (Ihmels et al. 2002) have noted that each node can belong to more than one module depending on the biological state of the cell, or the context, and have correspondingly reexamined the clustering problem. Elemento et al. (2007) have recently presented a general information theoretic approach to inferring regulatory modules and the associated transcription factor binding sites from various kinds of high-throughput data. While clustering methods have been widely applied in the exploration of gene expression, it should be emphasized that merely finding clusters does not by itself provide evidence for modularity. As noted above, the whole discussion would be much more satisfying if we had independent definitions of modularity and, we might add, clearly stated alternative hypotheses about the structure and dynamics of these networks.

Focusing on the functional aspect of the module, we often observe that the majority of the components of a system (for instance, a set of promoter sites or a set of genes regulating motility in bacteria) are conserved together across species. These observations support the hypothesis that the conserved components are part of a very tightly coupled sub-network which we might identify as a module. Bioinformatic tools can then use the combined sequence and expression data to give predictions about modules, as reviewed by Siggia (2005). Purely phylogenetic approaches that infer module components based on inter-species comparisons have also been productive and can extract candidate modules based only on phylogenetic footprinting, that is, studying the presence or absence of homologous genes across organisms and correlating their presence with hand annotated phenotypic traits (Slonim et al. 2006).

Robustness

Robustness refers to a property of the biological network such that some aspect of its function is not sensitive to perturbations of network parameters, environmental variables (e. g. temperature),

or initial state; see de Visser et al. (2003) for a review of robustness from an evolutionary perspective and Goulian (2004) for mechanisms of robustness in bacterial circuits. Robustness encompasses two very different ideas. One idea has to do with a general principle about the nature of explanation in the quantitative sciences: qualitatively striking facts should not depend on the fine tuning of parameters, because such a scenario just shifts the problem to understanding why the parameters are tuned as they are. The second idea is more intrinsic to the function of the system, and entails the hypothesis that cells cannot rely on precisely reproducible parameters or conditions and must nonetheless function reliably and reproducibly.

Robustness has been studied extensively in the chemotactic system of the bacterium *Escherichia coli*. The systematic bias to swim towards chemoattractants and away from repellents can only be sustained if the bacterium is sensitive to the spatial gradients of the concentration and not to its absolute levels. This discriminative ability is ensured by the mechanism of perfect adaptation, with which the proportion of bacterial straight runs and tumbles (random changes in direction) always returns to the same value in the absence of gradients (Block et al. 1983). Naively, however, the ability to adapt perfectly seems to be sensitive to the amounts of intracellular signaling proteins, which can be tuned only approximately by means of transcriptional regulation. Barkai and Leibler (1997) argued that there is integral feedback control in the chemotactic circuit which makes it robust against changes in these parameters, and Alon et al. (1999) showed experimentally that precision of adaptation truly stays robust, while other properties of the systems (such as the time to adapt and the steady state) show marked variations with intracellular signaling protein concentrations.

One seemingly clear example of robust biological function is embryonic development. We know that the spatial structure of the fully developed organism follows a ‘blueprint’ laid out early in development as a spatial pattern of gene expression levels. von Dassow et al. (2000) studied one part of this process in the fruit fly *Drosophila*, the

‘segment polarity network’ that generates striped patterns of expression. They considered a dynamical system based on the wiring diagram of interactions among a small group of genes and signaling molecules, with ~ 50 associated constants parametrizing production and degradation rates, saturation response and diffusion, and searched the parameter space for solutions that reproduce the known striped patterns. They found that, with their initial guess at network topology, such solutions do not exist, but adding a particular link – biologically motivated though unconfirmed at the time – allowed them to find solutions by random sampling of parameter space. Although they presented no rigorous measure for the volume of parameter space in which correct solutions exist, it seems that a wide variety of parameter choices and initial conditions indeed produce striped expression patterns, and this was taken to be a signature of robustness.

Robustness in dynamical models is the ability of the biological network to sustain its trajectory through state space despite parameter or state perturbations. In circadian clocks the oscillations have to be robust against both molecular noise inherent in transcriptional regulation, examined in stochastic simulations by Gonze et al. (2002), as well as variation in rate parameters (Stelling et al. 2004); in the latter work the authors introduce integral robustness measures along the trajectory in state space and argue that the clock network architecture tends to concentrate the fragility to perturbations into parameters that are global to the cell (maximum overall translation and protein degradation rates) while increasing the robustness to processes specific to the circadian oscillator. As was mentioned earlier, robustness to state perturbations was demonstrated by Li et al. (2004) in the threshold binary network model of the yeast cell cycle, and examined in scale-free random Boolean networks by Aldana and Cluzel (2003).

As with modularity, robustness has been somewhat resistant to rigorous definitions. Importantly, robustness has always been used as a relational concept: function X is robust to variations in Y . An alternative to robustness is for the organism to exert precise control over Y , perhaps even using

X as a feedback signal. This seems to be how neurons stabilize a functional mix of different ion channels (Marder and Bucher 2006), following the original theoretical suggestion of LeMasson et al. (1993). Pattern formation during embryonic development in *Drosophila* begins with spatial gradients of transcription factors, such as Bicoid, which are established by maternal gene expression, and it has been assumed that variations in these expression levels are inevitable, requiring some robust readout mechanism. Recent measurements of Bicoid in live embryos, however, demonstrate that the absolute concentrations are actually reproducible from embryo to embryo with $\sim 10\%$ precision (Gregor et al. 2007a). While there remain many open questions, these results suggest that organisms may be able to exert surprisingly exact control over critical parameters, rather than having compensation schemes for initially sloppy mechanisms. The example of ion channels alerts us to the possibility that cells may even ‘know’ which combinations of parameters are critical, so that variations in a multidimensional parameter space are large, but confined to a low dimensional manifold.

Noise

A dynamical system with constant reaction rates, starting repeatedly from the same initial condition in a stable environment, always follows a deterministic time evolution. When the concentrations of the reacting species are low enough, however, the description in terms of time (and possibly space) dependent concentration breaks down, and the stochasticity in reactions, driven by random encounters between individual molecules, becomes important: on repeated trials from the same initial conditions, the system will trace out different trajectories in the state space. As has been pointed out in the section on stochastic dynamics, biological networks in this regime need to be simulated with the Gillespie algorithm (Gillespie 1977), or analyzed within approximate schemes that treat noise as perturbation of deterministic dynamics. Recent experimental developments have made it possible to observe this noise directly, spurring new research in the field. Noise in biological networks fundamentally limits the

organism's ability to sense, process and respond to environmental and internal signals, suggesting that analysis of noise is a crucial component in any attempt to understand the design of these networks. This line of reasoning is well developed in the context of neural function (Bialek 1987), and we draw attention in particular to work on the ability of the visual system to count single photons, which depends upon the precision of the G-protein mediated signaling cascade in photo receptors; see, for example, (Ramanathan et al. 2005).

Because transcriptional regulation inherently deals with molecules, such as DNA and transcription factors, that are present at low copy numbers, most noise studies were carried out on transcriptional regulatory elements. The availability of fluorescent proteins and their fusions to wild type proteins have been the crucial tools, enabling researchers to image the cells expressing these probes in a controllable manner, and track their number in time and across the population of cells. Elowitz et al. (2002) pioneered the idea of observing the output of two identical regulatory elements driving the expression of two fluorescent proteins of different colors, regulated by a common input in a single *Escherichia coli* cell. In this 'two-color experiment,' the correlated fluctuations in both colors must be due to the *extrinsic* fluctuations in the common factors that influence the production of both proteins, such as overall RNA polymerase or transcription factor levels; on the other hand, the remaining, uncorrelated fluctuation is due to the *intrinsic* stochasticity in the transcription of the gene and translation of the messenger RNA into the fluorescent protein from each of the two promoters (Swain et al. 2002). Ozbudak et al. (2002) have studied the contributions of stochasticity in transcription and translation to the total noise in gene expression in prokaryotes, while Pedraza and van Oudenaarden (2005) and Hooshangi et al. (2005) have looked at the propagation of noise from transcription factors to their targets in synthetic multi-gene cascades. Rosenfeld et al. (2005) have used the statistics of binomial partitioning of proteins during the division of *Escherichia coli* to convert their fluorescence measurements into the corresponding

absolute protein concentrations, and also were able to observe the dynamics of these fluctuations, characterizing the correlation times of both intrinsic and extrinsic noise.

Theoretical work has primarily been concerned with disentangling and quantifying the contributions of different steps in transcriptional regulation and gene expression to the total noise in the regulated gene (Paulsson 2004; Swain 2004; Thattai and van Oudenaarden 2001), often by looking for signatures of various noise sources in the behavior of the measured noise as a function of the mean expression level of a gene. For many of the examples studied in prokaryotes, noise seemed to be primarily attributable to the production of proteins in bursts from single messenger RNA molecules, and to pulsatile and random activation of genes and therefore bursty translation into mRNA (Golding et al. 2005). In yeast (Blake et al. 2003; Raser and O'Shea 2005) and in mammalian cells (Raj et al. 2006) such stochastic synthesis of mRNA was modeled and observed as well. Simple scaling of noise with the mean was observed in ~40 yeast proteins under different conditions by Bar-Even et al. (2006) and interpreted as originating in variability in mRNA copy numbers or gene activation.

Bialek and Setayeshgar (2005) have demonstrated theoretically that at low concentrations of transcriptional regulator, there should be a lower bound on the noise set by the basic physics of diffusion of transcription factor molecules to the DNA binding sites. This limit is independent of (possibly complex, and usually unknown) molecular details of the binding process; as an example, cooperativity enhances the 'sensitivity' to small changes in concentration, but doesn't lower the physical limit to noise performance (Bialek and Setayeshgar 2006). This randomness in diffusive flux of factors to their 'detectors' on the DNA must ultimately limit the precision and reliability of transcriptional regulation, much like the randomness in diffusion of chemoattractants to the detectors on the surface of *Escherichia coli* limits its chemotactic performance (Berg and Purcell 1977). Interestingly, one dimensional diffusion of transcription factors along the DNA can have a big impact on the speed with which TFs find

their targets, but the change in noise performance that one might expect to accompany these kinetic changes is largely compensated by the extended correlation structure of one dimensional diffusion (Tkačik and Bialek 2007). Recent measurements of the regulation of the *hunchback* gene by Bicoid during early fruit fly development by Gregor et al. (2007a) have provided evidence for the dominant role of such input noise, which coexists with previously studied output noise in production of mRNA and protein (Tkačik et al. 2008c). These results raise the possibility that initial decisions in embryonic development are made with a precision limited by fundamental physical principles.

Dynamics, Attractors, Stability and Large Fluctuations

The behavior of a dynamical system as the time tends to infinity, in response to a particular input, is interesting regardless of the nature of the network model. Both discrete and continuous, or deterministic and noisy, systems can settle into a number of fixed points, exhibit limit-cycle oscillations, or execute chaotic dynamics. In biological networks it is important to ask whether these qualitatively different outcomes correspond to distinct phenotypes or behaviors. If so, then a specific stable gene expression profile in a network of developmental genes, for example, encodes that cell's developmental fate, as the amount of lambda repressor encodes the state of lysis vs lysogeny switch in the phage. The history of the system that led to the establishment of a specific steady state would not matter as long as the system persisted in the same attractor: the dynamics could be regarded as a 'computation' leading to the final result, the identity of the attractor, with the activities of genes in this steady state in turn driving the downstream pathways and other modules; see Kauffman (1969) for genetic networks and Hopfield (1982) for similar ideas in neural networks for associative memory. Alternatively, such partitioning into transient dynamics and 'meaningful' steady states might not be possible: the system must be analyzed as a whole while it moves in state space, and parts of it do

not separately and sequentially settle into their attractors.

It seems, for example, that qualitative behavior of the cell cycle can be understood by progression through well-defined states or checkpoints: after transients die away, the cell cycle proteins are in a 'consistent' state that regulates division or growth related activities, so long as the conditions do not warrant a new transition into the next state (Chen et al. 2000; Nasmyth 1996). In the fruit fly *Drosophila* development it has been suggested that combined processes of diffusion and degradation first establish steady-state spatial profiles of maternal morphogens along the major axis of the embryo, after which this stable 'coordinate system' is read out by gap and other downstream genes to generate the body segments. Recent measurements by Gregor et al. (2007b) have shown that there is a rich dynamics in the Bicoid morphogens concentration, prompting Bergmann et al. (2007) to hypothesize that perhaps downstream genes read out and respond to morphogens even before the steady state has been reached. On another note, an interesting excitable motif, called the "feedback resistor," has been found in HIV Tat system – instead of having a bistable switch like the λ phage, HIV (which lacks negative feedback capability) implements a circuit with a single stable 'off' lysogenic state, that is perturbed in a pulse of trans activation when the virus attacks. The pulse probably triggers a threshold-crossing process that drives downstream events, and subsequently decays away; the feedback resistor is thus again an example of a dynamic, as opposed to the steady-state, readout (Weinberger and Shenk 2007). Excitable dynamics are of course at the heart of the action potential in neurons, which results from the coupled dynamics of ion channel proteins, and related dynamical ideas are now emerging other cellular networks (Süel et al. 2006).

If attractors of the dynamical system correspond to distinct biological states of the organism, it is important to examine their stability against noise-induced spontaneous flipping. Bistable elements are akin to the 'flip-flop' switches in computer chips – they form the basis of cellular (epigenetic) memory. While this mechanism for

remembering the past is not unique – for example, a very slow, but not bistable, dynamics will also retain ‘memory’ of the initial condition through protein levels that persist on a generation time scale (Sigal et al. 2006), it has the potential to be the most stable mechanism. The naturally occurring bistable switch of the λ phage was studied using stochastic simulation by Arkin et al. (1998), and a synthetic toggle switch was constructed in *Escherichia coli* by Gardner et al. (2000). Theoretical studies of systems where large fluctuations are important are generally difficult and restricted to simple regulatory elements, but Bialek (2001) has shown that a bistable switch can be created with as few as tens of molecules yet remain stable for years. A full understanding of such stochastic switching brings in powerful methods from statistical physics and field theory (Roma et al. 2005; Sasai and Wolynes 2003; Walczak et al. 2005), ultimately with the hope of connecting to quantitative experiments (Acar et al. 2005).

Optimization Principles

If the function of a pathway or a network module can be quantified by a scalar measure, it is possible to explore the space of networks that perform the given function optimally. An example already given was that of maximizing the growth rate of the bacterium *Escherichia coli*, subject to the constraints imposed by the known metabolic reactions of the cell; the resulting optimal joint usage of oxygen and food could be compared to the experiments (Ibarra et al. 2002). If enough constraints exist for the problem to be well posed, and there is sufficient reason to believe that evolution drove the organism towards optimal behavior, optimization principles allow us to both tune the otherwise unknown parameters to achieve the maximum, and also to compare the wild type and optimal performances.

Dekel and Alon (2005) have performed the cost/benefit analysis of expressing *lac* operon in bacteria. On one hand *lac* genes allow *Escherichia coli* to digest lactose, but on the other there is the incurred metabolic cost to the cell for expressing them. That the cost is not negligible to the bacterium is demonstrated best by the fact that it shuts off the operon if no lactose

is present in the environment. The cost terms are measured by inducing the *lac* operon with changeable amount of IPTG that provides no energy in return; the benefit is measured by fully inducing *lac* with IPTG and supplying variable amounts of lactose; both cost and benefit are in turn expressed as the change in the growth rate compared to the wild-type grown at fixed conditions. Optimal levels of *lac* expression were then predicted as a function of lactose concentration and bacteria were evolved for several hundred generations to verify that evolved organisms lie close to the predicted optimum.

Zaslaver et al. (2004) have considered a cascade of amino-acid biosynthesis reactions in *Escherichia coli*, catalyzed by their corresponding enzymes. They have then optimized the parameters of the model that describes the regulation of enzyme gene expression, such that the total metabolic cost for enzyme production was balanced against the benefit of achieving a desired metabolic flux through the biosynthesis pathway. The resulting optimal on-times and promoter activities for the enzymes were compared to the measured activities of amino-acid biosynthesis promoters exposed to different amino-acids in the medium. The authors conclude that the bacterium implements a ‘just-in-time’ transcription program, with enzymes catalyzing initial steps in the pathway being produced from strong and low-latency promoters.

In signal transduction networks the definition of an objective function to be maximized is somewhat more tricky. The ability of the cell to sense its environment and make decisions, for instance about which genes to up- or down-regulate, is limited by several factors: scarcity of signals coming from the environment, perhaps because of the limited time that can be dedicated to data collection; noise inherent in the signaling network that degrades the quality of the detected signal; (sub-) optimality of the decision strategy; and noise in the effector systems at the output. A first idea would be to postulate that networks are designed to lower the noise, and intuitively the ubiquity of mechanisms such as negative feedback (Becskei and Serrano 2000; Goulian 2004) is consistent with such an objective. There are various definitions for noise, however, which in addition are

generally a function of the input, raising serious issues about how to formulate a principled optimization criterion.

When we think about energy flow in biological systems, there is no doubt that our thinking must at least be consistent with thermodynamics. More strongly, thermodynamics provides us with notions of efficiency that place the performance of biological systems on an absolute scale, and in many cases this performance really is quite impressive. In contrast, most discussions of information in biological systems leave “information” as a colloquial term, making no reference to the formal apparatus of information theory as developed by Shannon and others more than fifty years ago (Shannon 1948). Although many aspects of information theory that are especially important for modern technology (e. g., sophisticated error-correcting codes) have no obvious connection to biology, there is something at the core of information theory that is vital: Shannon proved that if we want to quantify the intuitive concept that “ x provides information about y ,” then there is only one way to do this that is guaranteed to work under all conditions and to obey simple intuitive criteria such as the additivity of independent information. This unique measure of “information” is Shannon’s mutual information. Further, there are theorems in information theory which, in parallel to results in thermodynamics, provide us with limits to what is possible and with notions of efficiency.

There is a long history of using information theoretic ideas to analyze the flow of information in the nervous system, including the idea that aspects of the brain’s coding strategies might be chosen to optimize the efficiency of coding, and these theoretical ideas have led directly to interesting experiments. The use of information to think about cellular signaling and its possible optimization is more recent (Tkačik et al. 2008a; Ziv et al. 2006). An important aspect of optimizing information flow is that the input/output relations of signaling devices must be matched to the distribution of inputs, and recent measurements on the control of *hunchback* by Bicoid in the early fruit fly embryo (Gregor et al. 2007a) seem remarkably consistent with the (parameter free) predictions from these matching relations (Tkačik et al. 2008b).

In the context of neuroscience there is a long tradition of forcing the complex dynamics of signal processing into a setting where the subject needs to decide between a small set of alternatives; in this limit there is a well developed theory of optimal Bayesian decision making, which uses prior knowledge of the possible signals to help overcome noise intrinsic to the signaling system; Libby et al. (2007) have recently applied this approach to the *lac* operon in *Escherichia coli*. The regulatory element is viewed as an inference module that has to ‘decide,’ by choosing its induction level, if the environmental lactose concentration is high or low. If the bacterium detects a momentarily high sugar concentration, it has to discriminate between two situations: either the environment really is at low overall concentration but there has been a large fluctuation; or the environment has switched to a high concentration mode. The authors examine how plausible regulatory element architectures (e. g. activator vs repressor, cooperative binding etc.) yield different discrimination performance. Intrinsic noise in the *lac* system can additionally complicate such decision making, but can be included into the theoretical Bayesian framework.

The question of whether biological systems are optimal in any precise mathematical sense is likely to remain controversial for some time. Currently opinions are stronger than the data, with some investigators using ‘optimized’ rather loosely and others convinced that what we see today is only a historical accident, not organizable around such lofty principles. We emphasize, however, that attempts to formulate optimization principles require us to articulate clearly what we mean by “function” in each context, and this is an important exercise. Exploration of optimization principles also exposes new questions, such as the nature of the distribution of inputs to signaling systems, that one might not have thought to ask otherwise. Many of these questions remain as challenges for a new generation of experiments.

Evolvability and Designability

Kirschner and Gerhart (1998) define *evolvability* as an organism’s capacity to generate heritable phenotypic variation. This capacity may have

two components: first, to reduce the lethality of mutations, and second, to reduce the number of mutations needed to produce phenotypically novel traits. The systematic study of evolvability is hard because the genotype-to-phenotype map is highly nontrivial, but there have been some qualitative observations relevant to biological networks. Emergence of *weak linkage* of processes, such as the co-dependence of transcription factors and their DNA binding sites in metazoan transcriptional regulation, is one example. Metazoan regulation seems to depend on combinatorial control by many transcription factors with weak DNA-binding specificities and the corresponding binding sites (called cis-regulatory modules) can be dispersed and extended on the DNA. This is in stark contrast to the strong linkage between the factors and the DNA in prokaryotic regulation or in metabolism, energy transfer or macromolecular assembly, where steric and complementarity requirements for interacting molecules are high. In protein signaling networks, strongly conserved but flexible proteins, like calmodulin, can bind weakly to many other proteins, with small mutations in their sequence probably affecting such binding and making the establishment of new regulatory links possible and perhaps easy.

Some of the most detailed attempts to follow the evolution of network function have been by Francois and coworkers (Francois and Hakim 2004; Francois et al. 2007). In their initial work they showed how simple functional circuits, performing logical operations or implementing bistable or oscillatory behavior, can be reliably created by a mutational process with selection by an appropriate fitness function. More recently they have considered fitness functions which favor spatial structure in patterns of gene expression, and shown how the networks that emerge from dynamics in this fitness landscape recapitulate the outlines of the segmentation networks known to be operating during embryonic development.

Instead of asking if there *exists* a network of nodes such that they perform a given computation, and if it can be found by mutation and selection as in the examples above, one can ask how many network topologies perform a given computation.

In other words, one is asking whether there is only one (fine tuned?) or many topologies or solutions to a given problem. The question of how many network topologies, proxies for different genotypes, produce the same dynamics, a proxy for phenotype, is a question of designability, a concept originally proposed to study the properties of amino-acid sequences comprising functional proteins, but applicable also to biological regulatory networks (Nochomovitz and Li 2006). The authors examine three- and four-node binary networks with threshold updating rule and show that all networks with the shared phenotype have a common ‘core’ set of connections, but can differ in the variable part, similar to protein folding where the essential set of residues is necessary for the fold, with numerous variations in the nonessential part.

Future Directions

The study of biological networks is at an early stage, both on the theoretical as well as on the experimental side. Although high-throughput experiments are generating large data sets, these can suffer from serious biases, lack of temporal or spatial detail, and limited access to the component parts of the interacting system. On a theoretical front, general analytical insights that would link dynamics with network topology are few, although for specific systems with known topology computer simulation can be of great assistance. There can be confusion about which aspects of the dynamical model have biological significance and interpretation, and which aspects are just ‘temporary variables’ and the ‘envelope’ of the proverbial back-of-the-envelope calculations that cells use to perform their biological computations on; which parts of the trajectory are functionally constrained and which ones could fluctuate considerably with no ill-effects; how much noise is tolerable in the nodes of the network and what is its correlation structure; or how the unobserved, or ‘hidden,’ nodes (or their modification/activity states) influence the network dynamics.

Despite these caveats, cellular networks have some advantages over biological systems of comparable complexity, such as neural networks. Due

to technological developments, we are considerably closer to the complete census of the interacting molecules in a cell than we are generally to the picture of connectivity of the neural tissue. Components of the regulatory networks are simpler than neurons, which are capable of a range of complicated behaviors on different time-scales. Modules and pathways often comprise smaller number of interacting elements than in neural networks, making it possible to design small but interesting synthetic circuits. Last but not least, sequence and homology can provide strong insights or be powerful tools for network inference in their own right.

Those of us who come from the traditionally quantitative sciences, such as physics, were raised with experiments in which crucial elements are isolated and controlled. In biological systems, attempts at such isolation may break the regulatory mechanisms that are essential for normal operation of the system, leaving us with a system which is in fact more variable and less controlled than we would have if we faced the full complexity of the organism. It is only recently that we have seen the development of experimental techniques that allow fully quantitative, real time measurements of the molecular events inside individual cells, and the theoretical framework into which such measurements will be fit still is being constructed. The range of theoretical approaches being explored is diverse, and it behooves us to search for those approaches which have the chance to organize our understanding of many different systems rather than being satisfied with models of particular systems. Again, there is a balance between the search for generality and the need to connect with experiments on specific networks. We have tried to give some examples of all these developments, hopefully conveying the correct combination of enthusiasm and skepticism.

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Fluctuation Theorems, Brownian Motors and Thermodynamics of Small Systems

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Article Outline

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Glossary

Trajectory or path A crucial concept in the statistical description of small system is that of a trajectory or path. A path is the time sequence of configurations followed by the system as it is driven to a non-equilibrium state by the action of an external perturbation.

Control parameter External perturbations are usually described in terms of the control parameter λ . These are a set of external parameters (e.g. an electric field, magnetic field, optical force, ...) that can be experimentally controlled and do not fluctuate. Experimentally, control parameters are produced by macroscopic systems that are used to manipulate the small system under study and which are insensitive to thermal fluctuations (but that

produce other sorts of uncontrolled instrumental noises and drift effects).

Single molecule experiments (SME) Recent technological developments have provided the tools to design and build scientific instruments of high enough sensitivity and precision to manipulate and visualize individual molecules and measure microscopic forces. Using SME it is possible to manipulate molecules one at a time and measure distributions describing molecular properties, characterize the kinetics of biomolecular reactions, and detect molecular intermediates. SME provide the additional information about thermodynamics and kinetics of biomolecular processes. This complements information obtained in traditional bulk assays. In SME it is also possible to measure small energies and detect large Brownian deviations in biomolecular reactions, thereby offering new methods and systems to scrutinize the basic foundations of statistical mechanics. Common single molecule experimental techniques are: atomic-force microscopy, laser optical tweezers, magnetic tweezers and single-molecule fluorescence.

Free energy The natural or spontaneous evolution of any thermodynamic process is determined by the free energy. The free energy in thermodynamics is the equivalent of the mechanical energy in classical mechanics. Spontaneous transformations take place by a decrease of the free energy in the system. In addition, mechanical work must be exerted by an external agent upon the system to increase its free energy. For reversible processes the amount of work is equal to the free energy change. However, in general, processes are irreversible and the work must be always larger than the free energy difference (a statement of the second law of thermodynamics). Free energies in small systems are typically expressed in either work (pN·nm) or energy units (kJ/mol, kcal/mol or $k_B T$ where k_B is the Boltzmann constant and T is a reference temperature – usually 298 K or 25 degrees Celsius). The conversion factors are ($T = 298$ K): $1 k_B T$

$$= 4.11 \text{ pN} \cdot \text{nm} = 4.1110^{-21} \text{ J}, 1 k_B T = 0.6 \text{ kcal/mol} = 2.4 \text{ kJ/mol}.$$

ATP Acronym for adenosine triphosphate, the molecule that carries the energy necessary to sustain life processes. ATP is made of one adenosine base weakly bonded to three phosphate groups. Upon conversion (by hydrolysis) to ADP (adenosine diphosphate) and inorganic phosphate or AMP (adenosine monophosphate) and pyrophosphate (P-P), ATP delivers a considerable amount of free energy (in the range 8–12 kcal/mol, depending on buffer conditions). By coupling to other reactions, ATP hydrolysis supplies the energy necessary to carry out unfavorable transformations.

RNA RNA (ribonucleic acid) is a very important player in molecular biology that shows biological functions in between those attributed to DNA and proteins. For the biophysicist and the statistical physicist RNA is also a fascinating molecule. Primarily found in nature in single stranded form, RNA folds into a three dimensional structure mainly stabilized by stacking interactions and hydrogen bonds between complementary bases (A-U,G-C). Full complementarity between different RNA segments is often impossible so, at difference with DNA, RNA structure includes also mismatches between bases as well other structural defects (bulges, loops, junctions, ...). In addition to Watson-Crick base pairing, RNA forms a compact structure through specific interactions mediated by magnesium ions that bring together distal RNA segments.

Definition of the Subject

The thermodynamics of small systems describes energy exchange processes between a system and its environment in the low energy range of a few $k_B T$ where Brownian fluctuations are dominant (Bustamante et al. 2005). The main goal of this discipline is to identify the building blocks of a general theory describing energy fluctuations in non-equilibrium processes occurring in systems ranging from condensed matter physics to biophysics.

Thermodynamics, a scientific discipline inherited from the eighteenth century, is facing new challenges in the description of non-equilibrium small (sometimes also called mesoscopic) systems. Thermodynamics is a discipline built in order to explain and interpret energetic processes occurring in macroscopic systems made out of a large number of molecules on the order of the Avogadro number. The subsequent development of statistical mechanics has provided a solid probabilistic basis to thermodynamics and increased its predictive power at the same time. The development of statistical mechanics goes together with the establishment of the molecular hypothesis. Matter is made out of interacting molecules in motion. Heat, energy and work are measurable quantities that depend on the motion of molecules. The laws of thermodynamics operate at all scales.

However, thermodynamics, a science inherited in the eighteenth century from the times of the industrial revolution, has been inspired by motors and steam engines that proved to be indispensable during that time. It is fair then to question the relevance and applicability of all this knowledge when scientists immerse into the realm of the very small, far from the initial context that inspired Carnot and others.

What are the novel features of thermodynamics when applied to small (also called mesoscopic) systems? Is it necessary to revisit some of the main concepts that we learned from standard thermodynamics? How are energy dissipation and efficiency related for non-equilibrium small systems where energy fluctuations are dominant? Finally, what are the implications in quantum systems already governed by quantum fluctuations? Answering such questions is one of the main goals of this new discipline.

Introduction

The *non-equilibrium thermodynamics of small systems* is becoming quite popular among statistical physicists who recognize there new aspects of thermodynamics where large Brownian fluctuations are of pivotal importance as compared to

fluctuations in macroscopic (or large) systems. In macroscopic systems, fluctuations represent just small deviations respect to the average behavior. For example, an ideal gas of N molecules in thermal contact with a bath at temperature T has an average total kinetic energy of $(3/2)Nk_B T$. However, the total energy is not a conserved quantity but fluctuates, its spectrum being a Gaussian distribution of variance $(3/2)N(k_B T)^2$ according to the law of equipartition. Therefore, relative deviations of the energy are on the order $1/\sqrt{N}$ respect to the average value. For macroscopic systems such deviations are very small: for $N = 10^{12}$ (this is the typical number of molecules in a 1 ml test tube at nanomolar concentration) relative deviations are on the order of 10^{-6} , hence experimentally unobservable by calorimetry methods. For a few molecules, $N \sim O(1)$, relative deviations are on the same order. Fluctuations are then measurable by direct observation of individual molecules.

Small systems share the property that energy fluctuations are much larger than $\sim \sqrt{E}$ (the prediction by the law of large numbers) where E is the average total energy. Large deviations from average values are normally observed in mesoscopic systems where non-equilibrium fluctuations are governed by a few degrees of freedom. Examples abound in physics and biology: the Brownian motion of a micron-size silica bead captured in an optical trap; the unfolding of a bio-molecule (e.g. a nucleic acid hairpin or a protein); the movement of molecular motors inside the cell; the cooperative rearrangement of a nanosized region containing a few molecules inside an amorphous material such as a glass.

As a rule of thumb we can say that small systems are those where the typical energy content of the system is a few times $k_B T$, maybe from 1 to 1000 but not much more. As often happens, there is no well defined frontier separating the small-size regime from the large-size regime. The name thermodynamics of small systems was first coined by T. L. Hill (1994) who showed the importance of the statistical ensemble in thermodynamic relations. A main result of statistical mechanics is the independence of the equation of state on the statistical ensemble in the thermodynamic limit. Such independence breaks down in

small systems due to the contribution of fluctuations which depend on the type of statistical ensemble considered. In biology, the most important aspect of these tiny machines is that they operate far from equilibrium; its consequences and importance in their biological function are still unknown. The combination of small size and non-equilibrium behavior is the playground for the striking behavior observed in condensed matter physics and biophysics.

Prominent in the field is the study of the so called work and heat fluctuations in systems driven to a non-equilibrium state. Fluctuation theorems are mathematical relations that quantify the relative probability of trajectories that release and absorb a given amount of work/heat to and from the environment. Taken individually, the work and heat along these trajectories can violate some of the inequalities of thermodynamics, leading to what is commonly referred as *transient violations of the second law*. This name has raised strong objections among some groups of physicists. Of course the second law remains inviolate. The name just stresses the fact that Brownian fluctuations are big enough for such deviations from the average value to be observed. For macroscopic systems these trajectories are known to be irrelevant and unobservable, however at the level of small system sizes, when the energies involved are of order of several times $k_B T$, these trajectories become important. Although thermodynamic inequalities are known to describe the behavior of average values, it is important to explore the implications and relevance of these deviations in our understanding of energy transformation processes at the molecular level.

The quantitative experimental observation and measurement of large energy fluctuations has become possible only recently with the development of new micro-manipulation tools. Particularly important are the application of single-molecule techniques to explore physical theories in systems out of equilibrium. The use of new micro-manipulation tools in the exploration of the behavior of tiny objects (such as bio-molecules and motors) embedded in a thermal environment opens the possibility to investigate how these systems exchange energy with their

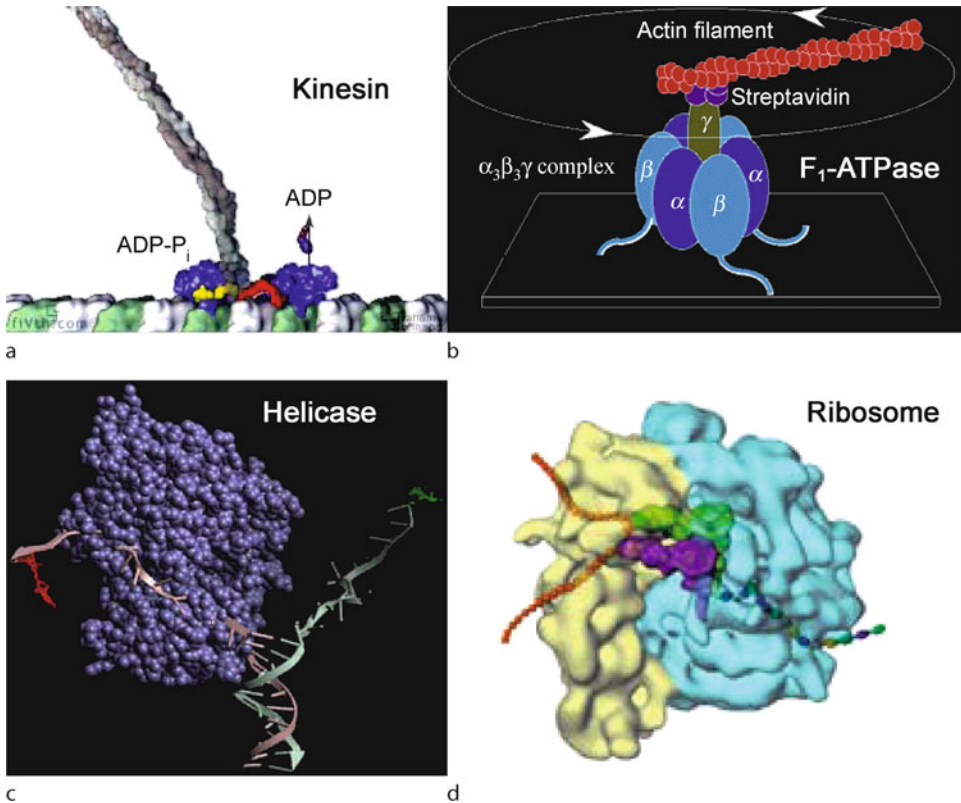
environment. This question is of great interest both at a fundamental and practical level. From a fundamental point of view, the comprehension of how bio-molecules operating very far from equilibrium are so efficient raises the question whether such tiny systems exploit rare and large deviations from their average behavior by rectifying thermal fluctuations from the bath. From a practical point of view, this might help in the design of efficient nanomotors in the future.

In the next sections we overview a selection of topics in this fascinating area of research. We will start by discussing molecular motors in section “[Molecular Motors](#)”. In section “[Non-equilibrium Thermodynamics of Small Systems](#)” we explain what are the main types of non-equilibrium states and introduce the microscopic definitions of heat

and work. In subsection “[The Jarzynski Equality](#)” we derive the Jarzynski equality by using the master equation approach. This part is a bit technical and the reader who is not interested in the details can jump to Eq. (17) and continue reading from there. Finally, in section “[Fluctuation Theorems](#)” we discuss fluctuation theorems and review some of their applications to condensed matter physics and biophysics. The article finishes with a discussion of future directions in research.

Molecular Motors

Molecular motors are proteins that use the energy extracted from the hydrolysis of ATP to exert mechanical work (Fig. 1) (Spudich 2002). The



Fluctuation Theorems, Brownian Motors and Thermodynamics of Small Systems, Fig. 1 Examples of molecular machines: (a) Kinesin walking a long microtubule and transporting a cargo. (b) F_1 -ATP synthase is the proton pump responsible of producing ATP in the mito-

chondria of eukaryotic cells. (c) Helicases are forerunners of the DNA polymerase that unwind DNA by transforming dsDNA into two strands of ssDNA. (d) The ribosome is one among the largest molecular machines inside the cytoplasm of the cell in charge of manufacturing proteins

mechanism by which motors utilize the energy stored in the high energy bonds of the ATP molecules to perform mechanical work is based on two hypothesized mechanisms: 1) Power stroke generation or 2) Brownian ratchet mechanism. In the first mechanism the release of the pyrophosphate during the ATP hydrolysis cycle is tightly coupled to the generation of force which drives the motor. In the second mechanism, the motor diffuses reversibly along the substrate. Movement is then produced by the hydrolysis of ATP that induces a conformational change in the protein. This change is then rectified by thermal fluctuations that induce the release of ADP. By steady repetition of this mechanochemical cycle (one ATP molecule is hydrolyzed per cycle) the motor carries out important cellular functions. Motors are characterized by the so called processivity or number of turnover cycles the motor does until detaching from the substrate. Processivities of molecular motors can vary by several orders of magnitude depending on the type of motor and the presence of other regulating factors. For example, the muscle myosin II motors work in large assemblies, each myosin having a processivity around 1, meaning that each myosin performs one mechanochemical cycle on average before detaching from the substrate. In the other extreme of the scale there are DNA polymerases in eukaryotes which show processivities that range from 1 (adding approximately one nucleotide before detaching) up to several thousands or even millions. However, in the presence of sliding clamps (proteins with the shape of a doughnut that encircle the DNA and tightly bind DNA polymerases) processivities go up to 10^9 . Molecular motors are magnificent objects from the point of view of their efficiency. If we define the efficiency rate as the ratio between the useful work performed by the motor and the energy released in the hydrolysis of one ATP molecule in one mechanochemical cycle, then typical values for the efficiencies are around several tens per cent, reaching the value of 90% in some cases (like in the rotary motor F_1 -ATPase). For example, out of the $20 k_B T$ obtained from the hydrolysis of one molecule of ATP, kinesin exerts a mechanical work of $12 k_B T$ at every step, having an efficiency of around 60%.

Such large efficiencies are rarely found in macroscopic systems (motors of cars have efficiencies below 20%) meaning that molecular motors have been designed by evolution to efficiently operate in a highly noisy environment. Molecular motors are expected to be essential constituents of future nanodevices.

What is the relation between molecular motors and the non-equilibrium thermodynamics of small systems? It is a well established fact that the typical amounts of energy obtained from chemical sources (e.g. ATP or GTP hydrolysis) used by most molecular machines are a few kcal per mol (at $T \sim 300$ K this corresponds to a few units of $k_B T$, $1 k_B T \simeq 0.6$ kcal/mol). Let us consider the example of RNA transcription. The process by which RNA nucleotides (A,U,G,C) are added to the newly synthesized RNA strand during the transcription process involves the hydrolysis of the different nucleoside-phosphate complexes as they are added to the 3' end of the growing chain. The overall process by which one base is added to the newly synthesized strand is a highly favorable reaction (mainly driven by the hydrolysis of the pyrophosphate) with a free energy release, ΔG , in the range between 7 and 12 kcal/mol mainly depending on the magnesium concentration in the environment. Effectively this is an irreversible process that generates an amount of available energy between 10 and $20 k_B T$ at room temperature (~ 300 K, $1 k_B T \simeq 0.6$ kcal/mol) per base pair added. This energy would be lost to the environment in the form of heat were it not for the fact that a big part of the energy is used by the RNA polymerase to locally unwind the double DNA helix and pull apart the two DNA strands to produce a bubble a few bases long of denatured DNA. This bubble is then used by the DNA/RNA/polymerase ternary complex as a substrate to polymerize the RNA. As transcription proceeds the bubble moves downstream together with the RNA polymerase and the RNA transcript is synthesized.

For this process to occur, the RNA polymerase must move against the Stokes friction produced by water as well as other roadblocks that hamper its motion. In particular, the RNA polymerase must exert force and torque on the DNA. Typical

forces to unzip DNA are on the order of 15 pN meaning that the minimum mechanical work necessary to unzip one base pair is around 15 pN times 12 Angstroms (the typical extension gained after pulling apart two bases at the fork of a DNA hairpin), which is equal to 18 pN · nm or equivalently $4.4 k_B T$ ($1 k_B T \simeq 4.11 \text{ pN} \cdot \text{nm}$ at room temperature). We can define the efficiency of the RNA motor as the ratio between the mechanical work needed to unzip one base pair and the amount of energy obtained from hydrolysis upon the addition of a nucleotide (however this is not the only way to define mechanical efficiencies, e.g. see Wang and Oster 2002; Bustamante et al. 2004). The efficiency of the transcription process is then about 40%, a quite remarkable feat if we compare this number with the ones obtained in man made machines (cars have efficiencies below 20%). The motion of a single RNA polymerase has been studied in several prokaryotic systems using optical and magnetic tweezers (Yin et al. 1995; Wang et al. 1998). In these experiments a DNA/polymerase complex is tethered between a trapped bead and an streptavidin coated immobilized bead or surface. To initiate transcription nucleotides are allowed to flow inside the chamber and the elongation of the transcript can be followed in real time while force is applied on the tether. The extension of the RNA transcript as a function of time reveals a complex intermittent motion of the polymerase with pauses (temporary stops), arrests (permanent stops) and even backtracking events (Davenport et al. 2000; Forde et al. 2002).

Non-equilibrium Thermodynamics of Small Systems

Non-equilibrium States

An important concept in thermodynamics is the state variable. State variables are those that, once determined, uniquely specify the thermodynamic state of the system. Examples are the temperature, the pressure, the volume and the mass of the different components in a given system. To specify the state variables of a system it is common to put the system in contact with a bath. The bath is

any set of sources (of energy, volume, mass, etc.) large enough to remain unaffected by the interaction with the system under study. The bath ensures that a system can reach a given temperature, pressure, volume and mass concentrations of the different components when put in thermal contact with the bath (i.e. with all the relevant sources). Equilibrium states are then generated by putting the system in contact with a bath and waiting until the system properties relax to the equilibrium values. Under such conditions the system properties do not change with time and the average heat/work/mass exchanged between the system and the bath is zero.

Non-equilibrium states can be produced in many ways, either by continuously changing the parameters of the bath or by preparing the system in an initial nonequilibrium state that slowly relaxes toward equilibrium. In general a non-equilibrium state is produced whenever the system properties change with time and/or the net heat/work/mass exchanged by the system and the bath is non zero. We can distinguish at least three different classes of non-equilibrium states:

- **Non-equilibrium transient state (NETS)** The system is initially prepared in an equilibrium state and later driven out of equilibrium by switching on an external perturbation. The system quickly returns to a new equilibrium state once the external perturbation stops changing.

A classic example of NETS is the case of a protein in its initial native state that is mechanically pulled (e.g. using AFM) by exerting force on the ends of the molecule. The protein is initially folded and in thermal equilibrium with the surrounding aqueous solvent. Upon pulling the protein is driven away from equilibrium into a transient state until it finally settles into the unfolded and extended equilibrium state. Another example of a NETS is a bead immersed in water and trapped in an optical well generated by a focused laser beam. When the trap is moved to a nearby new position (e.g. by moving the laser beams) the bead is driven to a NETS. After some time the bead reaches equilibrium again at the new position of the trap. In another experiment the trap

is suddenly put in motion at a speed v so the bead is transiently driven away from its equilibrium average position until it settles into a non-equilibrium steady-state (NESS, see below) characterized by the speed of the trap. The average position of the bead lags behind the position of the center of the trap.

- **Non-equilibrium steady-state (NESS)** The system is driven by external forces (either time dependent or non-conservative) in a stationary non-equilibrium state where its properties do not change with time. The steady state cannot be described by the Boltzmann-Gibbs distribution and the average net heat that is dissipated by the system (equal to the entropy production of the bath) is positive.

A classic example of a NESS is an electrical circuit made out of a battery and a resistance. The current flows through the resistance and the chemical energy stored in the battery is dissipated to the environment in the form of heat; the average dissipated power, $\mathcal{P}_{\text{dis}} = VI$, is equal to the power supplied by the battery. Another example is a sheared fluid between two plates or coverslips and one of them is moved relative to the other at a constant velocity v . To sustain such state a mechanical power equal to $\mathcal{P} \propto \eta v^2$ has to be exerted upon the moving plate where η is the viscosity of water. The mechanical work produced is then dissipated in the form of heat through the viscous friction between contiguous fluid layers. Further examples of NESS are chemical reactions in metabolic pathways that are sustained by activated carrier molecules such as ATP. In such cases, hydrolysis of ATP is strongly coupled to specific oxidative reactions. For example, ionic channels use ATP hydrolysis to transport protons against the electromotive force.

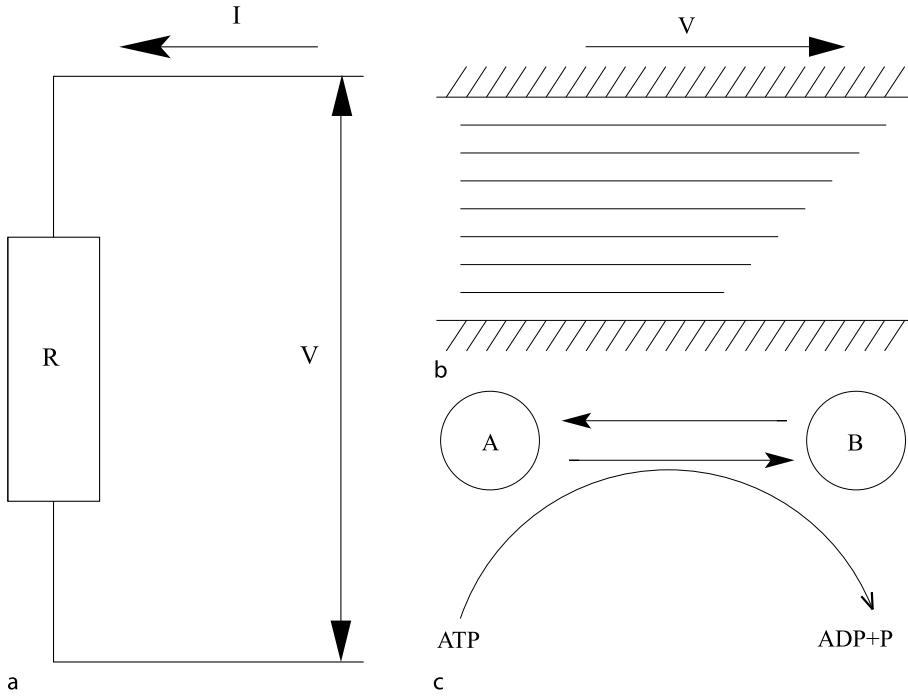
- **Non-equilibrium aging state (NEAS)** The system is initially prepared in a non-equilibrium state and put in contact with the sources. However, at difference with NETS, the system fails to reach thermal equilibrium in observable or laboratory time scales. In this case the system is in a non-stationary slowly

relaxing non-equilibrium state called *aging state* and characterized by a very small entropy production of the sources. In the aging state two-time correlations decay slower as the system becomes older. Two-time correlation functions depend on both times and not just on their difference. The classic example of a NEAS is a super-cooled liquid cooled below its glass transition temperature (Ediger et al. 1996). The liquid solidifies into an amorphous slowly relaxing state characterized by huge relaxational times and anomalous low frequency response. Other systems are colloids that can be prepared in a NEAS by the sudden reduction/increase of the volume fraction of the colloidal particles or by putting the system under a strain/stress (Cipelletti and Ramos 2005).

The classes of non-equilibrium states previously described do not make distinctions whether the system is macroscopic or small. In small systems, however, it is common to speak about the control parameter to emphasize the importance of the constraints imposed by the bath that are externally controlled and do not fluctuate. The control parameter (λ) represents a value (in general, a set of values) that defines the state of the bath. Its value determines the equilibrium properties of the system, e.g. the equation of state. In macroscopic systems it is unnecessary to discern which value is externally controlled because fluctuations are small and all equilibrium ensembles give the same equivalent thermodynamic description, i.e. the same equation of state. Differences arise when taking into account fluctuations. The non-equilibrium behavior of small systems is then strongly dependent on the specific non-equilibrium protocol. Figure 2 shows a representation of a few examples of NESS and control parameters.

Microscopic Definitions of Work and Heat

Microscopic definitions of work and heat can be given using Markov processes. Let us consider a general system described by an energy function $E(C)$ where C is a generic configuration in contact with a bath at temperature T . For instance, in a gas



Fluctuation Theorems, Brownian Motors and Thermodynamics of Small Systems, Fig. 2 Examples of NESS: (a) An electric current I flowing through a resistance R and maintained by a voltage source or control parameter V . (b) A fluid sheared between two plates that

move at speed v (the control parameter) relative to each other. (c) A chemical reaction $A \rightarrow B$ coupled to ATP hydrolysis. The control parameters are the concentrations of ATP and ADP

of N molecules, C would stand for their positions and momenta. The dynamics are assumed to be discrete in time with elementary time-step Δt . A trajectory or path of the system is characterized by the sequence of configurations

$$\begin{aligned} \Gamma &\equiv \{C_k; 0 \leq k \leq M\} \\ &\equiv \{C_0, C_1, C_2, \dots, C_M\} \end{aligned} \quad (1)$$

where k is the index for the discrete time step and M is the total number of time steps. The time corresponding to step k is then given by $t = k\Delta t$ with $t = 0$ ($k = 0$) and t_f ($k = M/\Delta t$) denoting the initial and final times respectively. The continuous-time limit is recovered by taking $\Delta t \rightarrow 0$, $M \rightarrow \infty$ with t_f finite.

Now we will treat the case where the system is perturbed in a prescribed way. Because the dynamics is stochastic, it will generate an ensemble of trajectories when the same experiment is

repeated many times. In addition to the configuration C , and in order to characterize the perturbation protocol, we need to specify the temporal sequence of values $\{\lambda_k; 0 \leq k \leq M\}$. The control parameter λ shifts the energy levels of the system according to the relation,

$$E_\lambda(C) = E(C) - \lambda A(C) \quad (2)$$

where $A(C)$ is the observable coupled to the external perturbation λ (e.g., if λ is a magnetic or gravitational field then A stands for the magnetization or the height of the center of mass respectively).

We now consider the variation of energy along a given path $\Delta E(\Gamma) = E_{\lambda_f}(C_f) - E_{\lambda_0}(C_0)$ where C_0, C_f are the initial and final configurations for that path and λ_0, λ_f are the initial and final values of the control parameter as defined by the protocol (path independent). From Eq. (2) the energy variation is given by,

$$\begin{aligned}\Delta E(\Gamma) &= E_{\lambda_M}(C_M) - E_{\lambda_0}(C_0) \\ &= \sum_{k=0}^{M-1} (E_{\lambda_{k+1}}(C_{k+1}) - E_{\lambda_k}(C_{k+1})) \\ &\quad - \sum_{k=0}^{M-1} (E_{\lambda_k}(C_k) - E_{\lambda_k}(C_{k+1}))\end{aligned}\quad (3)$$

with $\Delta\lambda_k = \lambda_{k+1} - \lambda_k$. This decomposition identifies work and heat by using the first law of thermodynamics, $\Delta E = W - Q$. The first term in Eq. (3) is identified as the work W exerted upon the system whereas the second corresponds to the heat Q transferred from the system to the bath,

$$W(\Gamma) = \sum_{k=0}^{M-1} (E_{\lambda_{k+1}}(C_{k+1}) - E_{\lambda_k}(C_{k+1})) \quad (4)$$

$$Q(\Gamma) = \sum_{k=0}^{M-1} (E_{\lambda_k}(C_k) - E_{\lambda_k}(C_{k+1})). \quad (5)$$

We concentrate our attention on the work exerted upon the system along a given path Γ . Inserting (2) in (4) we get

$$\begin{aligned}W(\Gamma) &= \sum_{k=0}^{M-1} \left(\frac{\partial E_{\lambda_k}(C_k)}{\partial \lambda} \right)_{\lambda=\lambda_k} \Delta\lambda_k \\ &= - \sum_{k=0}^{M-1} A(C_k) \Delta\lambda_k \equiv - \int_0^t ds \dot{\lambda}(s) A(C(s)) ds\end{aligned}\quad (6)$$

where we have applied the continuous-time limit in the last term in the r.h.s. of (6).

As the path is stochastic the work is a fluctuating quantity that can be characterized by its probability distribution $\mathcal{P}(W)$ defined as,

$$\mathcal{P}(W) = \sum_{\Gamma} P(\Gamma) \delta(W - W(\Gamma)) \quad (7)$$

where Γ stands for the path and $P(\Gamma)$ indicates the probability of that path. The importance of $\mathcal{P}(W)$ relies upon the fact that it is a quantity that is experimentally measurable and therefore is suitable to quantitatively characterize work fluctuations with the aid of recently developed micro-manipulation tools.

The Jarzynski Equality

In 1997 Chris Jarzynski derived a remarkable equality describing work fluctuations in non-equilibrium isothermal systems (Jarzynski 1997). This relation was somewhat unexpected because it related the free energy change in a reversible process with exponential averages of the work measured in irreversible processes. The equality applies to all non-equilibrium systems under general assumptions of local detailed balance and ergodicity. In what follows we show a derivation of the equality based on a master equation approach. The following calculation intends to show the simplicity of the algebraic math used in the derivation of this general result. The reader not interested in math details can jump directly to Eq. (17) and continue reading from there.

Let us consider a system in contact with a thermal bath at temperature T that is initially in thermal equilibrium. The system is then driven to a NETS under the action of an external perturbation described by the temporal sequence of values $\{\lambda_k; 0 \leq k \leq M\}$.

We consider the ensemble of all possible trajectories that start from an initial state characterized by the distribution $P_{\lambda_0}(C)$. Dynamics of the system are then given by the set of probabilities $P_{\lambda_k}(C)$ for the system to be found at configuration C at time-step k . These probabilities satisfy a master equation. For a Markov process the time evolution of the $P_{\lambda_k}(C)$ depends on the quantities, $\mathcal{W}_{\lambda_k}(C \rightarrow C')$, defined as the transition probability per unit time to go from configuration C to C' at time-step k . The $\mathcal{W}$'s are assumed to lead to an ergodic dynamics (where any pair of configurations are always connected by at least one trajectory, i.e. dynamics is *irreducible*) and satisfy the detailed balance condition,

$$\begin{aligned}\frac{\mathcal{W}_{\lambda_k}(C \rightarrow C')}{\mathcal{W}_{\lambda_k}(C' \rightarrow C)} &= \frac{P_{\lambda_k}^{\text{eq}}(C')}{P_{\lambda_k}^{\text{eq}}(C)} \\ &= \exp(-\beta(E_{\lambda_k}(C') - E_{\lambda_k}(C)))\end{aligned}\quad (8)$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant and T is the temperature. The $P_{\lambda_k}^{\text{eq}}(C)$ is the Boltzmann-Gibbs distribution,

$$P_{\lambda}^{\text{eq}}(C) = \exp(-\beta E_{\lambda}(C_0))/Z_{\lambda};$$

$$Z_{\lambda} = \sum_C \exp(\beta E_{\lambda}(C)) \quad (9)$$

where $Z_{\lambda} = \exp(-\beta F_{\lambda})$ is the partition function and F_{λ} is the free energy.

The energy function $E_{\lambda_k}(C)$ is given in (2). Under very general conditions these dynamics guarantee that the system reaches a stationary state where configurations are populated according to the Boltzmann–Gibbs weight. The solution to the master equation gives the time evolution for the system.

For a generic path-dependent observable $\mathcal{A}(\Gamma)$, the ensemble average value is given by,

$$\langle \mathcal{A} \rangle = \sum_{\Gamma} P(\Gamma) \mathcal{A}(\Gamma). \quad (10)$$

Using the fact that the dynamics are Markovian together with the definition (1) we can write,

$$P(\Gamma) = P_{\lambda_0}^{\text{eq}}(C_0) \prod_{k=0}^{M-1} \mathcal{W}_{\lambda_k}(C_k \rightarrow C_{k+1}) \quad (11)$$

where the system initially starts in equilibrium at λ_0 . By inserting (11) into (10) we obtain,

$$\langle \mathcal{A} \rangle = \sum_{\Gamma} \mathcal{A}(\Gamma) P_{\lambda_0}^{\text{eq}}(C_0) \prod_{k=0}^{M-1} \mathcal{W}_{\lambda_k}(C_k \rightarrow C_{k+1}). \quad (12)$$

Using the detailed balance condition (8) this expression reduces to,

$$\langle \mathcal{A} \rangle = \sum_{\Gamma} P_{\lambda_0}^{\text{eq}}(C_0) \mathcal{A}(\Gamma) \prod_{k=0}^{M-1} \left[\mathcal{W}_{\lambda_k}(C_{k+1} \rightarrow C_k) \exp[-\beta(E_{\lambda_k}(C_{k+1}) - E_{\lambda_k}(C_k))] \right] \quad (13)$$

$$= \sum_{\Gamma} \mathcal{A}(\Gamma) P_{\lambda_0}^{\text{eq}}(C_0) \exp \left[-\beta \sum_{k=0}^{M-1} (E_{\lambda_k}(C_{k+1}) - E_{\lambda_k}(C_k)) \right] \prod_{k=0}^{M-1} \mathcal{W}_{\lambda_k}(C_{k+1} \rightarrow C_k). \quad (14)$$

This equation can not be worked out further for a general observable $\mathcal{A}$. However, let us consider the observable, $\mathcal{A}(\Gamma) = \exp(-W(\Gamma))$, where $W(\Gamma)$ stands for the work defined in (4). By inserting this expression in (14) we obtain the Jarzynski equality:

$$\langle \exp(-W) \rangle = \frac{1}{Z_{\lambda_0}} \sum_{\Gamma} \prod_{k=0}^{M-1} \mathcal{W}_{\lambda_k}(C_{k+1} \rightarrow C_k) \exp(-\beta E_{\lambda_M}(C_0))$$

$$= \frac{Z_{\lambda_M}}{Z_{\lambda_0}} = \exp(-\beta F_{\lambda_M} - F_{\lambda_0}) = \exp(-\beta \Delta F) \quad (15)$$

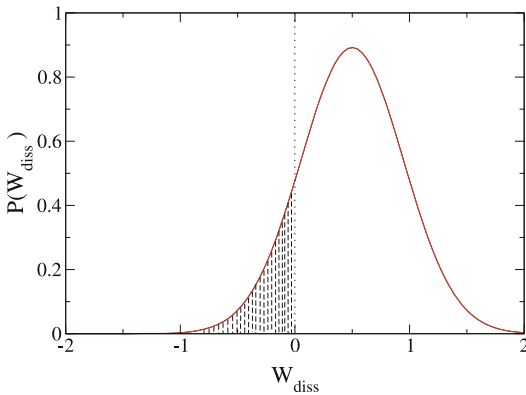
where we have applied a telescopic sum and used (9). To carry out the telescopic sums we first summed over $C_0, C_1 \dots$ by applying the normalization condition on the transition probabilities,

$$\sum_{C'} \mathcal{W}_k(C \rightarrow C') = 1. \quad (16)$$

The second law of thermodynamics, $\langle W \rangle \geq \Delta F$, also follows naturally as a particular case of (15) by using the convexity inequality, $\langle \exp(x) \rangle \geq \exp \langle x \rangle$. The Jarzynski equality is often written in the form,

$$\langle \exp(-W_{\text{diss}}) \rangle = 1 \quad (17)$$

where $W_{\text{diss}} = W - \Delta F$ is called the dissipated work. The second law of thermodynamics puts bounds on the minimum amount of average work performed on the system: although W may strongly fluctuate from path to path its mean value (averaged over an infinite number of repeated experiments, i.e. the first moment of $P(W)$) is always greater than the reversible or quasi-static work, W_{rev} , which is also equal to the free energy difference ΔF between the initial and final equilibrium states. The reversible work is the value of the work that is obtained for protocols that are adiabatic or quasi-static, i.e. the control parameters are changed infinitely slowly. The difference between the actual work and the reversible work then corresponds to the dissipated work, $W_{\text{diss}} = W - \Delta F$. The second law establishes that in



Fluctuation Theorems, Brownian Motors and Thermodynamics of Small Systems, Fig. 3 Probability distribution of the dissipated work: According to the second law of thermodynamics the average dissipated work is always positive. However, because of fluctuations, the dissipated work of some paths can be negative (shaded area). These paths are sometimes referred to as “transient violations of the second law”

average a positive amount of heat is irreversibly lost to the environment, $\langle W_{\text{diss}} \rangle \geq 0$ (Fig. 3). The amount of dissipation in irreversible processes is then related to the asymmetry between the phase space densities obtained when the process is run forward and backward in time (Kawai et al. 2007).

Gaussian work distributions exactly satisfy (17) provided the average dissipated work $\langle W_{\text{diss}} \rangle$ and the variance of the work, σ_W^2 , are related by $\sigma_W^2 = 2k_B T \langle W_{\text{diss}} \rangle$. A fluctuation-dissipation parameter R can be introduced to quantify deviations from the Gaussian behavior (Ritort et al. 2002),

$$R = \frac{\sigma_W^2}{2k_B T \langle W_{\text{diss}} \rangle}. \quad (18)$$

For Gaussian work distributions $R = 1$, corresponding to non-equilibrium processes in the linear regime where the fluctuation-dissipation theorem holds.

The validity of the Jarzynski equality extends to deterministic dynamics (e.g. Hamiltonian or thermostated). In Hamiltonian dynamics the set of phase space points then behaves as an incompressible fluid, a consequence of the Liouville theorem. The case of Hamiltonian dynamics was originally addressed by Jarzynski in his original

derivation of the non-equilibrium work relation (Jarzynski 1997). The stochastic case has been analyzed also for general Markov processes by Crooks (1999, 2000) and for Langevin dynamics by Kurchan (1998) and Seifert (2005a). Equation (15) has appeared in the past in the literature in the form of a generalized fluctuation-dissipation relation proposed by Bochkov and Kuzovlev (1981) which is mathematically identical to the Jarzynski equality (Jarzynski 1997). Related results to the Jarzynski’s equality can be also traced back also in the free-energy perturbation identity derived by Zwanzig (1954) and the Kirkwood formula (Kirkwood 1935).

Fluctuation Theorems

Since the beginning of the 90’s some exact results in statistical mechanics have provided a mathematical description of energy fluctuations (in the form of heat and work) for non-equilibrium systems. This new class of results go under the name of fluctuation theorems (FTs) and provide a solid theoretical basis to quantify energy fluctuations in non-equilibrium systems. FTs describe energy fluctuations in systems while they execute transitions between different types of states. For these fluctuations to be observable the system has to be small enough and/or operate over short periods of time, otherwise the measured properties approach the macroscopic limit where fluctuations get masked by the dominant average behavior. Most fluctuation theorems are of the form,

$$\frac{P(+S)}{P(-S)} = \exp\left(\frac{S}{k_B}\right), \quad (19)$$

where S has the dimensions of an entropy that may represent heat and/or work produced during a given time interval. The precise mathematical form of relations such as (19) (for instance, the precise definition of S or whether they are valid at finite time intervals or just in the limit where the time interval goes to infinity) depends on the particular non-equilibrium conditions (e.g. whether

the systems starts in an equilibrium Gibbs state, or whether the system is in a non-equilibrium steady state, or whether the system executes transitions between steady states, etc.).

Generally speaking, FTs relate the amounts of work or heat exchanged between the system and its environment for a given non-equilibrium process and its corresponding time-reversed process. The time-reversed process is defined as follows. Let us consider a given non-equilibrium process (we call it forward, denoted by F) characterized by the protocol $\lambda_F(t)$ of duration t_f . In the reverse process (denoted by R) the system starts at $t = 0$ in a stationary state at the value $\lambda_F(t_f)$ and the control parameter is varied for the same duration t_f as in the forward process according to the protocol $\lambda_R(t) = \lambda_F(t_f - t)$. FTs depend on the type of initial state and the particular type of dynamics (deterministic versus stochastic) or thermostated conditions.

Despite of the fact that most of these theorems are treated as distinct they are in fact closely related. The main hypothesis for all theorems is the validity of some form of microscopic reversibility or local detailed balance (see however Cohen and Mauzerall 2004, Jarzynski 2004, Astumian 2006 for some controversy). Major classes of FTs include the transient FT (TFT) and the steady state FT (SSFT):

- The transient FT (TFT) In the TFT the system initially starts in an equilibrium (Boltzmann-Gibbs) state and is driven away from equilibrium by the action of time-dependent forces that derive from a time-dependent potential $V_{\lambda(t)}$. The potential depends on time through the value of the control parameter $\lambda(t)$. At any time during the process the system is in an unknown transient non-equilibrium state. If the value of λ is kept fixed then the system relaxes into a new equilibrium state. The TFT was introduced by Evans and Searles (1994) in thermostatted systems and later extended by Crooks to Markov processes (Crooks 1999).
- The steady state FT (SSFT) In the SSFT the system is in a non-equilibrium steady state where it exchanges net heat and work with the environment. The existence of the SSFT was numerically anticipated by Evans and collaborators for thermostated systems (Cohen et al. 1993)

and demonstrated for deterministic Anosov systems by Gallavotti and Cohen (1995). The entropy production S by the system (equal to the heat exchanged by the system divided by the temperature of the environment) satisfies the relation (19) in the asymptotic limit of large times $t \rightarrow \infty$ and for bounded energy fluctuations, $\sigma = \frac{|S|}{t} < \sigma^*$ where σ^* is a model dependent quantity. Other classes of SSFTs include stochastic Langevin dynamics (Kurchan 1998), Markov chains (Lebowitz and Spohn 1999; Maes 1999) or the case where the system initially starts in a steady state (Oono and Paniconi 1998) and executes transitions between different steady states (Hatano and Sasa 2005; Speck and Seifert 2005a).

Particularly relevant to the single molecule context is the FT by Crooks (1999, 2000) which relates the work distributions measured along the forward (F) and reverse (R) paths,

$$\frac{P_F(W)}{P_R(-W)} = \exp\left(\frac{W - \Delta F}{k_B T}\right). \quad (20)$$

where $P_F(W)$, $P_R(-W)$ are the work distributions along the F and R processes respectively, and ΔF is the free energy difference between the equilibrium states corresponding to the final value of the control parameter $\lambda_f = \lambda(t_f)$ and the initial one $\lambda_i = \lambda(0)$. A particular result of (20) is the Jarzynski equality (Jarzynski 1997) described in subsection “The Jarzynski Equality” that is obtained from (20) by rewriting it as $P_R(-W) = \exp\left(\frac{-W + \Delta G}{k_B T}\right) P_F(W)$ and integrating both sides of the equation between $W = -\infty$ and $W = \infty$. Because of the normalization property of probability distributions, the left hand side is equal to 1 and the Jarzynski equality reads,

$$\left\langle \exp\left(-\frac{W}{k_B T}\right) \right\rangle_F = \exp\left(-\frac{\Delta F}{k_B T}\right) \text{ or } \Delta F = -k_B T \log \left(\left\langle \exp\left(-\frac{W}{k_B T}\right) \right\rangle_F \right). \quad (21)$$

where $\langle \dots \rangle_F$ denotes an average over an infinite number of paths, all generated by a given forward protocol $\lambda_F(t)$.

Experimental Tests and Free Energy Recovery

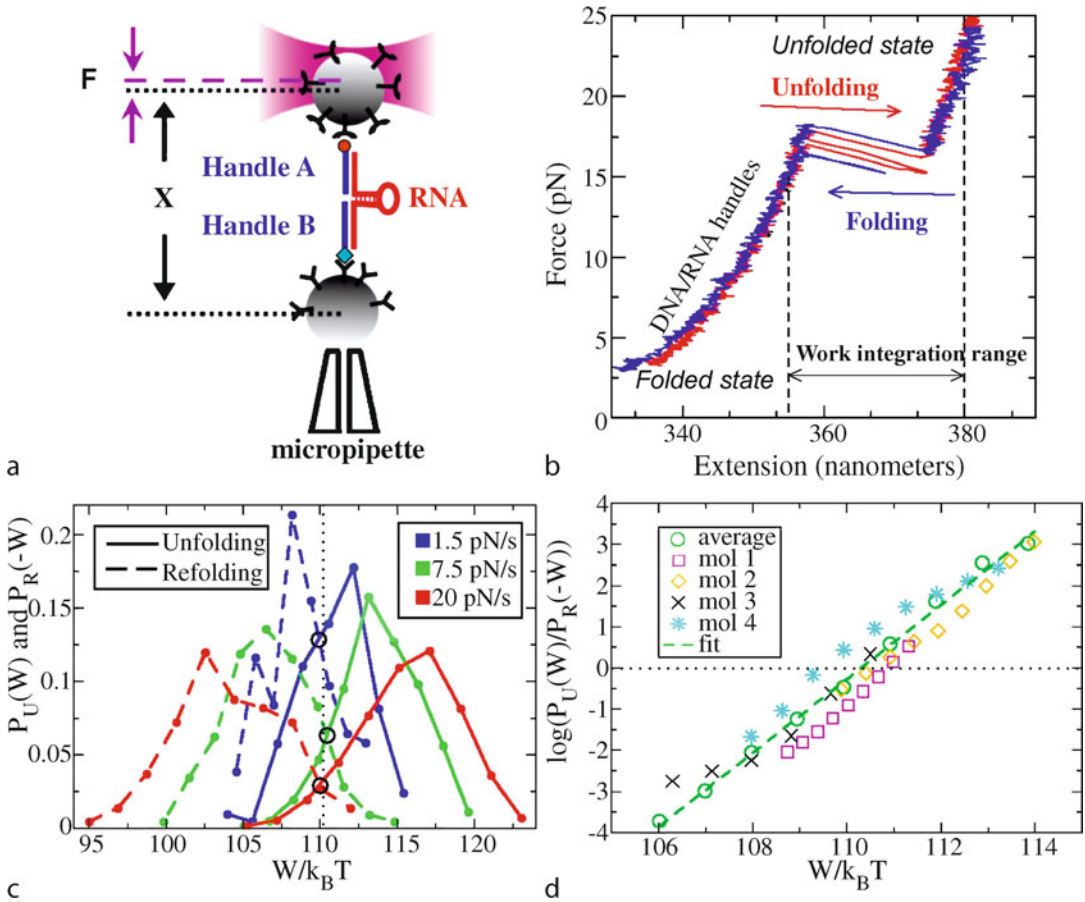
Various categories of FTs have been introduced and experimentally validated. The first experimental tests of FTs were carried out by Ciliberto and coworkers for the Gallavoti-Cohen FT in Rayleigh-Bernard convection (Ciliberto and Laroche 1998) and turbulent flows (Ciliberto et al. 2004). Later on FTs were tested for beads trapped in an optical potential and moved through water at low Reynolds numbers. The motion of the bead is then well described by a Langevin equation that includes a friction (non-conservative) force, a confining (conservative) potential and a source of stochastic noise. Experiments have been carried out by Evans and collaborators who have tested the validity of the TFT (Wang et al. 2002; Carberry et al. 2004), and by Liphardt and collaborators for a bead executing transitions between different steady states (Trepagnier et al. 2004). The validity of the TFT has been also recently tested for non-Gaussian optical trap potentials (Blickle et al. 2005).

The Jarzynski equality and the FT by Crooks can be used to recover equilibrium free-energy differences between different molecular states by using non-equilibrium measurements in single molecule experiments (Hummer and Szabo 2001; Jarzynski 2001; Hummer and Szabo 2005). In particular, by using the Jarzynski equality (21) it is possible to extract the value of ΔF from repeated measurements of the mechanical work along many trajectories. The idea is to repeat non-equilibrium experiments many times and evaluate the exponential average in the r.h.s of (21) to extract the work corresponding to the reversible process. Would it then not be easier to directly measure the work for a reversible process? Unfortunately many processes cannot be carried in quasistatic conditions (either simulations or experiments) and therefore, alternative methods are required to determine free-energy differences. There are practical difficulties in the applicability of (21) as the number of trajectories included in the exponential average must be actually infinite. This is unrealizable in practice as non-equilibrium experiments can be performed only a finite number of times and the finiteness of the number of trajectories introduces a bias. It is known that the number of trajectories required to evaluate the Jarzynski equality grows

exponentially with the average value of the dissipated work. The dependence of the bias and error with the number of pulls has been estimated in some cases (Zuckermann and Woolf 2002; Gore et al. 2003). In general this dependence can be quite complicated as it depends on the behavior of the low-work tails of the distribution $P(W)$ which are difficult to analyze in general.

In 2002, the Jarzynski equality was experimentally tested by pulling the P5ab RNA hairpin, a derivative of the *Tetrahymena Thermophila* L21 ribozyme (Liphardt et al. 2002) using optical tweezers. However, in that case the molecule was pulled not too far from equilibrium. The Jarzynski equality and related identities for athermal systems have been recently put under scrutiny in other systems (Schuler et al. 2005; Douarche et al. 2005a, b). The Jarzynski equality and the FT by Crooks have inspired several theoretical papers discussing other related exact results (Van Zon and Cohen 2003a, b; Seifert 2004; Jarzynski and Wojcik 2004; Seifert 2005b; Reid et al. 2005), free-energy recovery from numerical simulations (Hummer 2001; Isralewitz et al. 2001; Jensen et al. 2002; Park et al. 2003; Andriocioaei et al. 2003; Park and Schulten 2004), bias and error estimates for free-energy differences (Zuckermann and Woolf 2002; Gore et al. 2003; Bennett 1976; Wood et al. 1991; Hendrix and Jarzynski 2001; Shirts et al. 2003), enzyme kinetics (Qian 2005; Min et al. 2005) or solvable models (Mazonka and Jarzynski 1999; Lhua and Grossberg 2005; Bena et al. 2005; Speck and Seifert 2005b; Cleuren et al. 2007). In addition, analytical studies on small systems thermodynamics show that work/heat distributions display non-Gaussian tails describing large and rare deviations from the average and/or most probable behavior (Van Zon and Cohen 2004; Ritort 2004; Imparato and Peliti 2005a; Imparato and Peliti 2005b). These theoretical studies open the way to investigate the possible relevance of these large deviations in other non-equilibrium systems in condensed matter physics.

The FT by Crooks can be applied and tested by measuring the unfolding and refolding work distributions in single molecule pulling experiments (Fig. 4a). For example, let us consider the case of a molecule (e.g. a DNA or RNA hairpin



Fluctuation Theorems, Brownian Motors and Thermodynamics of Small Systems, Fig. 4 Experimental measurement of work fluctuations in small systems using single molecules. (a) Experimental setup in RNA force pulling experiments using optical tweezers. An RNA hairpin of a few tens of base pairs is inserted between two molecular handles (A and B) that are attached to two beads. One bead is trapped in the optical well, the other bead is immobilized on the tip of a micropipette. As the optical trap is moved relative to the micropipette the RNA molecule is stretched. (b) Measured force-extension cycle showing a force rip around 15pN characteristic of the unfolding/refolding of the RNA molecule. The work along a given unfolding/refolding force-extension curve

corresponds to the area below the curve integrated along a given range of the molecular extension (indicated by the two vertical dashed lines). (c) Work distributions for the unfolding and refolding process measured at three different pulling speeds. According to the FT by Crooks all curves should cross at a given value of the work, $W = \Delta F$, independently of the pulling speed. In this case $\Delta F \simeq 110k_B T$, a number that includes also the stretching contributions from the hybrid handles and the ssRNA. (d) Experimental verification of the FT by Crooks for four different tethered molecules (all with identical sequence). The black dashed line is the best fit for all curves and has slope equal to 0.9 ± 0.1 . Results taken from Collin et al. (2005)

or a protein) initially in thermal equilibrium in the folded (F) or native state. By applying mechanical force (e.g. using atomic force microscopy or optical tweezers) the molecule can be mechanically unfolded and the conformation of the molecule changed from the native to

the unfolded (U) state. The unfolding event is observed by the presence of a rip in the force-extension curve of the molecule (Fig. 4b). During the unfolding process the tip of the cantilever or the bead in the trap exerts a mechanical work on the molecule that is given by,

$$W = \int_{x_0}^{x_f} F dx \quad (22)$$

where x_0 , x_f are the initial and final extension of the molecule. In (22) we are assuming that the molecular extension x is the externally controlled parameter (i.e. $\lambda \equiv x$) which is not necessarily the case. However the corrections introduced by using (22) are shown to be often small. The work (22) done upon the molecule along a given path corresponds to the area below the force-extension curve that is limited by the initial and final extensions, x_0 and x_f (Fig. 4b). Because the unfolding of the molecule is a stochastic (i.e. random) process, the value of the force at which the molecule unfolds changes from experiment to experiment and so does the value of the mechanical work required to unfold the molecule. Upon repetition of the experiment many times a distribution of unfolding work values for the molecule to go from the folded (F) to the unfolded (U) state is obtained, $P_F \rightarrow_U(W)$. A related work distribution can be obtained if we reverse the pulling process by releasing the molecular extension at the same speed at which the molecule was previously pulled, to allow the molecule to go from the unfolded (U) to the folded (F) state. In that case the molecule refolds by performing mechanical work on the cantilever or the optical trap. Upon repetition of the folding process many times the work distribution, $P_U \rightarrow_F(W)$ can be also measured. The unfolding and refolding work distributions can then be measured in stretching/releasing cycles (Fig. 4c). From (20) we observe that $P_F(\Delta F) = P_U(-\Delta F)$ so the forward and reverse work probability distributions cross each other at $W = \Delta F$. In Fig. 4c we observe that both distributions cross each other at a value (ΔF) that is independent of the pulling speed as expected. Figure 4d shows the experimental verification of (20).

The FT by Crooks has been tested in different types of RNA molecules and the method has been shown capable of recovering free-energies under strong non-equilibrium conditions (Collin et al. 2005). The work probability distributions were measured along the unfolding and refolding

pathways for a three-way junction RNA molecule and found to strongly deviate from a Gaussian distribution (Collin et al. 2005). These experimental results pave the way for other related studies, for example in molecular dynamics simulations (Kosztin et al. 2006).

These kind of studies will expand in the future to cover more complex cases and other non-equilibrium situations such as the free-energy recovery of folding free energies in native states in proteins or free energies in misfolded structures and intermediate states in RNA molecules and proteins. Ultimately FTs, when combined with SME, will offer an excellent opportunity to characterize and understand the possible biological relevance of large deviations and extremal fluctuations in molecular systems.

Future Directions

The experimental and theoretical study of non-equilibrium small systems offers exciting possibilities for the statistical physicist and the biophysicist. This discipline aims to describe the novel properties observed in bio-molecules and molecular machines operating far from equilibrium, such as the folding of a nucleic acid or a protein or the trans-location motion of a molecular motor.

We are just starting to have a glance about how these small objects exchange energy with their environment. It is a well known fact in molecular biology and biochemistry that biological function at the molecular level is tightly related to structure. It might not be surprising that the link between molecular structure and biological function is encoded in the low frequency region of the spectrum of non-equilibrium energy fluctuations (the spectrum of energy fluctuations extending far at the most extreme tails of the distribution). It is difficult to imagine how bio-molecular processes, often carrying a lot of information, can operate solely from high frequency events describing the motion of a few number of atoms. Rather, these should somehow rely on the low frequency cooperative motion between different and distant parts

of the molecule. Investigating fluctuations in non-equilibrium systems calls for a deeper theoretical understanding of large deviation functions in non-equilibrium systems as well as more systematic and accurate experiments identifying sources of large energy fluctuations in biological systems.

We are at the dawn of an interdisciplinary scientific discipline that will bring together scientists with expertises coming from very different branches of knowledge. This merging process might culminate with the future engineering of artificial mesoscopic structures capable of reproducing and even improving the behavior of the biological ones.

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Neuronal Dynamics

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Article Outline

Glossary

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Glossary

Action potential or Spikes electrical pulses of an amplitude of about 100 mV that travel along nerve fibers.

Field potential an electrical signal recorded extracellularly which arises from the synchronized activity of many cells.

Hippocampus one of the most studied area of the mammalian nervous system which is part of the limbic system and is involved in learning and memory.

Neuron the main excitable cells of nerve tissue.

Network an ensemble of synaptically connected cells.

Synapse the specialized junction between two neurons where the action potential voltage transient in the presynaptic cell is transmitted to the post-synaptic cell via neurotransmitter release (chemical synapse) or direct electrical connection (electrical synapse).

Definition of the Subject

How information is processed by nervous systems is a question of major interest, with far-reaching implications for domains as diverse as medicine and philosophy. It is however still far from understood despite much work and progress during the last 60 years. Neurons are cells which exhibit diverse dynamical behaviors. Our present partial view makes it clear that, besides physiology of single neurons and anatomy of neural systems, understanding the dynamics of coupled neuron assemblies and their collective dynamics is of utmost importance. This requires supplementing the tools of experimental biology, that themselves are making impressive progress, by modeling and theoretical analysis.

Introduction

Since the first electrical recordings, it has been noted that the mammalian brain exhibits diverse patterns of activity [14]. Oscillations at various frequencies are prominent features of human electroencephalograms that is, voltage signals recorded from the scalp [19]. Their dominant frequencies are state and task dependent shifting from slow “delta” frequencies (1–4 Hz) in certain stages of sleep, to “alpha” frequencies (8–13 Hz) in quiet wakefulness or “beta” frequencies (13–30 Hz) in attentive immobility. Intracranial recordings of field potential or neuron activity in animals have revealed higher frequency components from 40 Hz to more than 200 Hz and have also shown that neural rhythms depend on the neural structures from which they originate [3]. For instance, in the rat hippocampus, rhythms at theta (4–8 Hz) and gamma (30–100 Hz) frequencies are observed during exploratory behaviors whereas intermittent fast oscillations (100–200 Hz) are recorded during awake immobility and consummatory behaviors [34]. In the rat olfactory bulb, odorants induce strong gamma oscillations [4].

Electrophysiological recordings, visualization, pharmacological and genetic manipulations are important experimental tools for observing and assessing the mechanisms underlying this complex neural activity. However, analyzing the dynamics of a large ensemble of coupled dynamical elements is a difficult task. Modeling, theoretical analysis and computer simulations are proving increasingly helpful to interpret experimental data, as it becomes more precise and extensive, and to direct further experiments.

In the following, we first review the different types of models that are currently most useful in analyzing network dynamics. We then consider various topics to which theoretical modeling has significantly contributed. We start in Sect. “Intrinsic Network Dynamics” by discussing spontaneous neural activity, that is, activity not directly induced by stimulus-processing. Experimentally, “background” spontaneous activity appears to consist of neurons firing irregularly and at low rates and poses a first modeling challenge. The coexistence of different attractors, a question of central interest in different contexts, is considered next. We then review the different mechanisms that are thought to give rise to the various time scales of neural dynamics. In Sect. “Stimulus Driven Dynamics”, we examine how stimulus presentation can modify neural dynamics and discuss various ways in which dynamics can lead to information processing. We begin by discussing two contrasting views: classically, sensory processing has been thought to proceed by a feedforward and stimulus-driven dynamic, whereas some more recent modeling and experiments suggest that stimuli provide only a weak bias on endogenous dynamics. We then examine various other ways in which dynamics can contribute to information processing and memory. The precise role of oscillations at diverse frequencies in information processing is still ill-understood. We briefly discuss two of the better understood structures and several proposals. We finally conclude, in Sect. “Future Directions”, by pointing out some approaches that appear to bear promises of future progress.

Types of Modeling and Theoretical Tools

The first task of a modeler in computational or theoretical neuroscience is to specify a particular model to be investigated. Choosing which model depends, of course, on the nature of the problem one is interested in, as well as on the availability of relevant experimental data. For example, if one is interested in understanding the origin of the irregularity of spike trains in cortex as observed in extracellular recordings *in vivo*, it is clear that one needs a spiking neuron model. For people working at the network level, this means specifying at least three things: the ‘architecture’ of the network (number of ‘units’, a specification of who communicates with who, and finally specification of the inputs); a model for the ‘units’ themselves (these ‘units’ can be groups or populations of functionally equivalent neurons, or single neurons); and a model for the connections between the units (synapses in the case units are single neurons). In this section, we first briefly describe popular models of units and connections, and then commonly studied network architectures. Finally, we explain briefly the theoretical methods that are used to investigate such networks.

Different Classes of Neurons Models

Broadly speaking, there are three classes of models: rate models; networks of binary neurons; and networks of spiking neurons. Though networks of binary neurons are a very useful tool to investigate associative memory properties of recurrent networks, they are not well-suited to study questions involving dynamics. We therefore restrict ourselves here to discussing rate models and networks of spiking neurons.

Rate Models In so-called ‘rate models’ (also called neural mass models, or neural field models), one describes the activity of a population of functionally equivalent neurons by a continuous variable r that typically obeys an ordinary differential equation. In its simplest form, the activity of a single population of neurons can be described by the equation

$$\tau \frac{dr}{dt} = -r + \Phi(I_{\text{ext}} + Jr), \quad (1)$$

where: r is the mean activity (firing rate) of the population, τ is the characteristic time constant of rate dynamics, Φ is the steady state input-output transfer function (f-I curve), that is typically taken to be sigmoidal, I_{ext} are the external inputs to the population, and J is the strength of the intra-population connections. For excitatory populations, $J > 0$, while for inhibitory populations, $J < 0$.

The function Φ that describes the ‘static’ transfer function of neurons in the population can take different forms. Popular transfer functions are threshold-linear,

$$\Phi(I) = \begin{cases} I - T & I > T \\ 0 & I < T \end{cases}, \quad (2)$$

where T is a threshold, or sigmoidal, $\Phi(I) = r_{\text{max}}/(1 + \exp(-\beta(I - T)))$, where T is again a threshold and β measures the steepness of the f-I curve at half-maximal firing rate. Note that while the threshold-linear transfer function is unbounded, the sigmoidal one saturates at a maximal rate r_{max} . In the limit $\beta \rightarrow \infty$, the sigmoidal transfer function becomes binary, $\Phi = r_{\text{max}}$ for $I > T$, $\Phi = 0$ otherwise.

Another choice is to take Φ as the analytically computed transfer function of a specific spiking neuron model, like the integrate-and-fire model. As described below, one can compute the average firing frequency as a function of both mean and variance of inputs in some simple cases, and the resulting function can be used as a transfer function in a rate model formulation [7]. Examples of f-I curves are shown schematically in Fig. 1a.

Spiking Neurons As for most cells, ionic concentration differences and selective membrane permeability make neurons intracellularly hyperpolarized with respect to the extracellular medium. The difference between the intracellular and extracellular potentials, the cell membrane potential, is thus negative, with a typical value of about -70 mV. Most neurons in the nervous systems of vertebrates use action

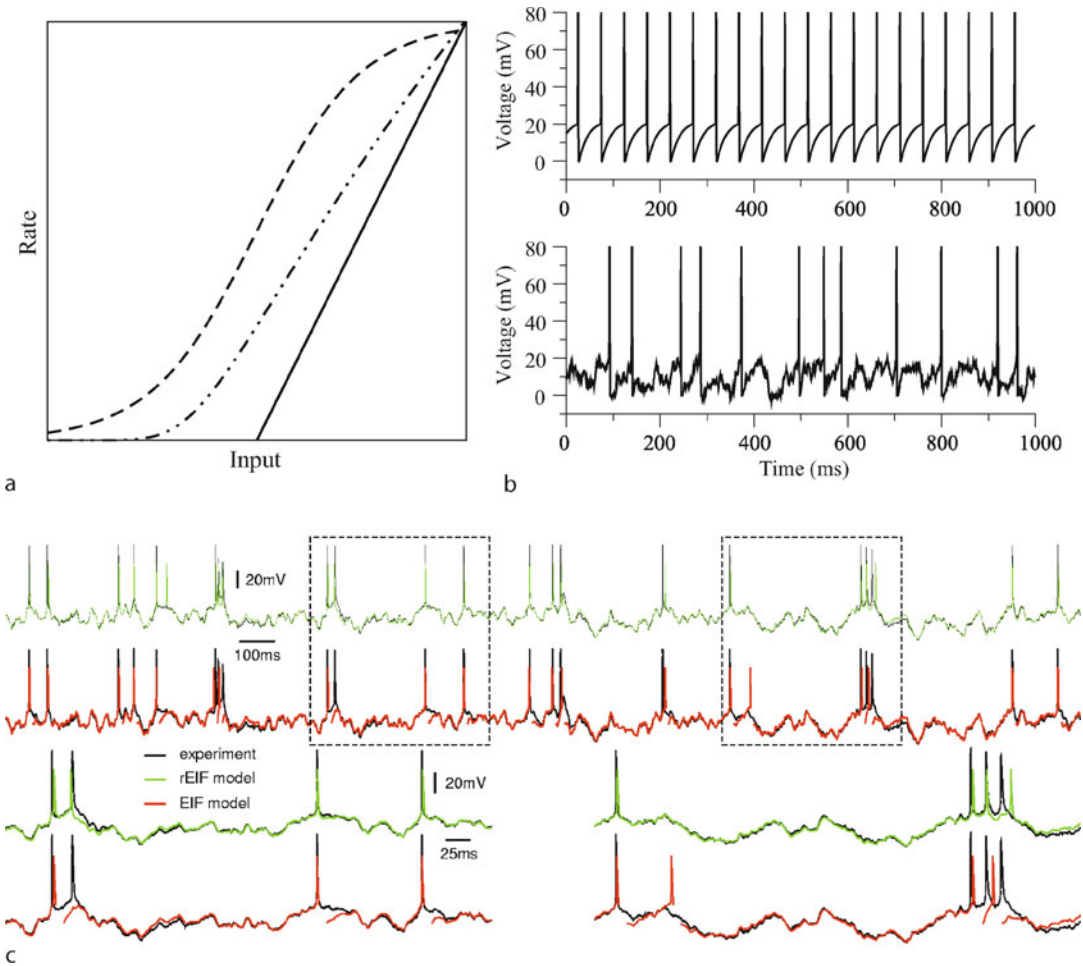
potentials,¹ or spikes, which are large depolarizations of short duration (~ 1 ms), as communication units. It is therefore natural to use spiking neuron models in network studies. The action potential is primarily a membrane phenomenon that can be described with different degrees of realism and refinement. There is a correspondingly large diversity of single neuron spiking models in the literature, from simple, one-variable integrate-and-fire models, to complex multi-compartmental models with many voltage-gated ionic channels. The complexity of a single neuron model can be characterized along two dimensions: (i) the number of variables describing the membrane dynamics at a given location; and (ii) the number of compartments describing the spatial geometry of the neuron.

Along the first dimension, the simplest model is the integrate-and-fire model. It retains as its only variable the membrane potential [27, 28, 68, 74, 112] and simply describes the action potential by a threshold V_T in membrane potential. In the subthreshold range $V < V_T$, the membrane dynamic is simply described as that of a capacitance C (of about $1 \mu\text{F}/\text{cm}^2$, coming from the insulating property of the lipid bilayer) in parallel with a passive leak conductance g ,

$$\tau_m \frac{dV}{dt} = -(V - V_L) + I_{\text{syn}}(t), \quad (3)$$

where $\tau_m = C/g$ is the membrane time constant (typical values are 10 – 20 ms), V_L is the resting potential, and $I_{\text{syn}}(t)$ are the synaptic inputs, in which we have absorbed the input resistance of the neuron (typical values are 10 – $100 M\Omega$). Thus, in Eq. (3), the inputs are in mV. In this model, a spike is emitted when the voltage hits the threshold V_T . At such times, the voltage is immediately reset to a sub-threshold voltage V_R . It is also possible to add to the model an absolute refractory period, during which the voltage is clamped to the reset, to get saturation of the firing frequency. To choose the values of the voltage parameters, there are basically two options: take the ‘realistic’

¹ Note however that there are well-documented exceptions, for instance in the retina.



Neuronal Dynamics, Fig. 1 Single unit/neuron models. (a) Rate model: commonly used f-I curves Φ (mean firing rate as a function of inputs). *Solid*: threshold linear function. *Dashed*: sigmoidal function. *Dot-dashed*: f-I curve of a leaky integrate-and-fire neuron subjected to noisy inputs. (b) Dynamics of a leaky integrate-and-fire neuron (membrane potential) driven by constant suprathreshold input (*upper panel*) or noisy input (*lower panel*). Spikes

are added by hand to better visualize the timing. (c) Dynamics of two versions of an exponential integrate-and-fire model (*red*: with hard reset, *green*: with adaptive threshold), together with recording of a cortical pyramidal cell. Both the artificial and the real cell receive the same injected time-dependent current (a realization of an Ornstein–Uhlenbeck process). (From Ref. [8])

values (similar to observed values in real neurons), $V_L \sim -70$ mV, $V_T \sim -50$ mV, and V_R somewhere in between; or define the origin of the voltage to be $V_L = 0$, and redefine V_T and V_R accordingly. The dynamic of the integrate-and-fire model to various types of inputs is shown in Fig. 1b.

At the opposite extreme, ‘biophysically realistic’ models aim to accurately represent the dynamics of the ionic channels that modify membrane

permeability. They often employ the celebrated Hodgkin–Huxley formalism [55] which describes the ionic channel contribution as changes in membrane conductance via the dynamics of the activation and inactivation of various voltage-gated ionic currents. While the integrate-and-fire model, due to its very simplicity, is a model of choice for analytical studies and large-scale simulations, it lacks many features exhibited by real neurons. These features can often be accurately

captured in the Hodgkin–Huxley formalism but at the price of difficulties in mathematical analysis (due to a large number of variables and pronounced non-linearities) and heavy computational cost. An intermediate class of models try to capture the best of both worlds: they contain the minimal number of variables (typically 1 or 2) and the minimal non-linearity required to capture particular phenomena of interest [21]. For example, generalized integrate-and-fire neurons contain an additional variable coupled to the voltage, which can give rise to sub-threshold resonance, as seen in many cell types [61, 104]; non-linear integrate-and-fire models can accurately capture spike generation with a minimal (exponential) non-linearity in the voltage equation [8, 42], see Fig. 1c; firing rate adaptation can be captured by a single adaptation variable coupled to the voltage; and so on.

Along the second (spatial) dimension, a similar diversity exists. The simplest models are composed of a single compartment. At the opposite, detailed models of cells with highly branched dendritic trees, such as the cerebellar Purkinje cell, can contain more than a thousand compartments [36]. Again, intermediate models, such as two-compartmental models, try to capture the best of both worlds: capturing non-trivial phenomena exhibited by real cells with the minimal description.

While multi-compartment models have been a valuable tool at the single neuron level, most studies of network behaviors use neurons with a single compartment. Apart from the obvious issues of mathematical tractability and computational cost, another concern limiting the use of such models is the limited present experimental knowledge on relative geometry and repartition of ionic channels. Ongoing initiatives, such as the “blue brain” project [86], may lead this to change, but we expect progress in this direction to be slow, given the huge number of parameters (especially if there are correlations in the properties of connected neurons).

Synapses

While in rate models synapses are specified by a single number, in spiking neuron models synapses are specified by dynamical variables. In the

simplest case, synapses have static amplitude: their response to a particular pre-synaptic spike is the same regardless of the history of their activation. However, many, if not all, synapses in the CNS are history-dependent. This is described by models capturing short- and/or long-term plasticity properties.

Total Synaptic Inputs A typical neuron in the CNS receives inputs from something on the order of 10,000 presynaptic neurons.² The total synaptic inputs $I_{\text{syn}}(t)$ of Eq. (3) are typically taken as a linear sum of both individual synaptic inputs and individual spikes. This leads to a synaptic current to neuron i of the type

$$I_i(t) = \sum_j J_{ij} \sum_k s(t - t_j^k),$$

where the sum over j runs over pre-synaptic neurons, J_{ij} defines the amplitude of a unitary post-synaptic potential (PSP) elicited by a spike of neuron j in neuron i ($J_{ij} > 0$ if neuron j is excitatory, while $J_{ij} < 0$ if neuron j is inhibitory), the sum over k is a sum over spikes of pre-synaptic neuron j , S describes the temporal dynamics of a unitary post-synaptic current (PSC see below), and t_j^k is the timing of the k th spike emitted by neuron j .

The simplest models use the so-called “current-based” description of synaptic inputs, in which the current is independent of the voltage. A more realistic description is to take a voltage dependent $J \propto g(V - V_{\text{rev}})$ where g is the time-dependent synaptic conductance, and V_{rev} is the corresponding reversal potential – the “conductance-based” description. Typical values for PSP amplitudes are in the range 0.1–1 mV; $V_{\text{rev}} \sim 0$ mV for excitatory synapses, while $V_{\text{rev}} \sim -80$ mV for inhibitory synapses. Typical values for synaptic conductances are in the nS range.

²This is an estimate for pyramidal cells in neocortex and hippocampus. Different cell types can have widely different average number of inputs, from the 4 average inputs of a granule cell in cerebellum, to the more than 100,000 inputs of a Purkinje cell.

A Simplified Semi-realistic Description for Single PSCs

The time course of post-synaptic currents elicited by a single spike can be described quite accurately by a delayed difference of exponentials. When a spike is emitted at time $t = 0$, the current is zero until $t = D$, where D is the delay, or latency, of the synaptic connection. Then the current is described by

$$s(t) \propto \exp\left(-\frac{(t-D)}{\tau_d}\right) - \exp\left(-\frac{(t-D)}{\tau_r}\right), \quad (4)$$

where $\tau_r < \tau_d$ describe the rise and decay times of the current, respectively. This can be equivalently described by the system of differential equations

$$\begin{aligned} \tau_d \frac{ds}{dt} &= -s + x \\ \tau_r \frac{dx}{dt} &= -x + \delta(t - D). \end{aligned}$$

Typical values for the time constants are: $D \sim 1$ ms; τ_r and τ_d vary widely depending on receptor type, but are $\tau_r < 1$ ms, $\tau_d \sim 2$ –10 ms for the fast (AMPA and GABA_A) receptor-mediated synaptic responses. See Fig. 2 for synaptic

currents described by Eq. (4), as well as a few experimentally recorded synaptic currents.

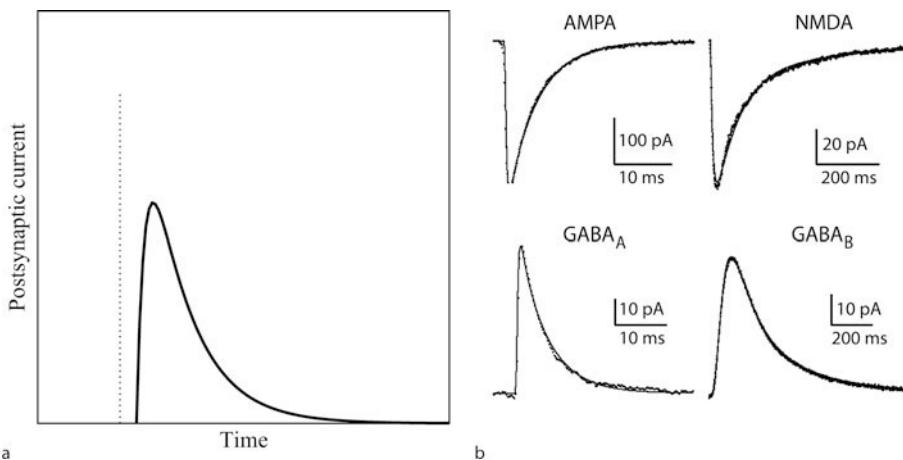
Dynamic Synapses Virtually all synapses in the CNS undergo plasticity at various time scales. Short-term plasticity (on timescales of 100 s of ms) is ubiquitous; Short-term depression and facilitation has been characterized experimentally and models exist that reproduce fairly accurately the characteristics of this plasticity (see [2, 117]).

On longer timescales (>1 h) various types of synapses (for example, pyramidal-to-pyramidal synapses in the neocortex; CA3 to CA1 synapses in the hippocampus; granule cell to Purkinje cell synapses in the cerebellum) exhibit various types of long-term plastic changes. There is a vast amount of material documenting such plasticity in the literature (for reviews see [16, 82, 83, 119]), and a large number of investigators have proposed models that account for rate-based and/or spike-timing based plasticity.

In this review, we will mostly consider networks with fixed synapses; the effects of both short-term and longterm plasticity will be mentioned only briefly.

Network Architecture

The network architecture specifies how the units, or neurons, are coupled together.



Neuronal Dynamics, Fig. 2 Synaptic models. (a) Synaptic current elicited by a single spike of Eq. (4). Timing of the presynaptic spike is indicated schematically by a dotted

line. (b) Synaptic currents mediated by various receptors, recorded in various slice preparations. From [38]

Architectures in Rate Models Rate models are often used to investigate the dynamics of spatially extended networks, or systems which encode continuous stimuli. A prototypical example is given by models of the primary visual cortex, in which the activity $r(x)$ at a given location x evolves according to

$$\tau \frac{dr(x)}{dt} = -r(x) + \Phi \left(I_{\text{ext}}(x, t) + \int dy J(x, y) r(y) \right). \quad (5)$$

The network ‘architecture’ is characterized by the ‘synaptic footprint’ $J(x, y)$ that specifies the strength of connections from y to x (the recurrent part); and the inputs $I_{\text{ext}}(x, t)$, describing inputs coming from outside the modeled network (LGN and other cortical areas in the case of primary visual cortex). See Fig. 3a.

Networks of Spiking Neurons The architecture of a network of spiking neurons can be specified by answering the following list of questions:

How many classes of neurons? Early studies of networks of spiking neurons focused on one population networks (either excitatory or inhibitory networks). Networks in which there are two populations of neurons—one excitatory, and one inhibitory—have also been analyzed in detail.

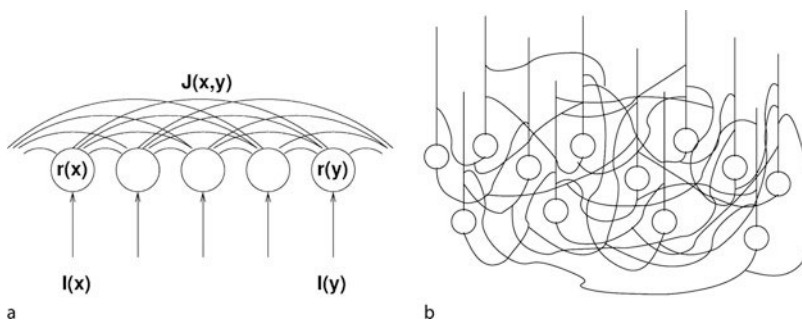
How many neurons in each class? Analytical studies often use the limit in which the number of neurons goes to infinity (see theoretical tools section below). This is justified by the fact that local networks in the brain are typically composed of a very large number of neurons ($\sim 10^5$). It is also becoming possible to simulate networks of such large numbers of neurons.

What is the wiring diagram? Early studies focused on fully connected networks, which are easier to handle analytically. Another popular architecture has been a randomly connected network, with a given connection probability (see Fig. 3b). Such an architecture takes into account the relatively low connection probability of nearby neurons. Relatively few studies of networks of spiking neurons take into account spatial structure, such as a monotonically decaying connection probability.

What is the nature of the individual couplings between neurons? Theorists have investigated networks connected by chemical synapses, electrical synapses, or both. More recently, the effect of various types of synaptic plasticity phenomena (both short-term and long-term) has begun to be studied.

What are the inputs to the neurons in the network?

Popular choices to study the intrinsic dynamics of networks are constant uniform inputs, or noisy inputs, which are uncorrelated from neuron to neuron. To understand the information



Neuronal Dynamics, Fig. 3 Network architectures. (a) Sketch of a rate model. Each circle represents a population of cells at a given location. Lines connecting circles represent synaptic connections between populations. (b)

A randomly connected network of individual neurons. The drawing schematically represents cell bodies (circles), dendrites (vertical line), and axons contacting dendrites of post-synaptic neurons (curved lines)

processing capabilities of networks, one has to choose a model for the type of inputs that are processed by such network. This choice typically depends on the area that is modeled. For example, inputs to a model of a hypercolumn in visual cortex are often taken to represent (fixed or dynamic) oriented bars, and are modeled appropriately.

Theoretical Tools

Different types of analytical tools are available depending on the nature of the model. Rate models are typically specified by systems of coupled ordinary differential equations. Hence, standard tools can be borrowed from dynamical system theory. One typically starts by investigating the case of constant inputs, for which it is sometimes possible to find fixed points, and the linear stability of these fixed points. Sometimes, it is possible to analyze more complex behaviors, oscillatory states, spatially localized states, waves, etc., and their stability.

Networks of spiking neurons are substantially harder to analyze. Several types of approximations can be used, depending on the strength of coupling and the level of noise: fully connected networks in the weak coupling/weak noise scenario can be studied in the framework of the theory of coupled oscillators. When coupling and noise are strong, it is sometimes possible to approximate synaptic inputs to a neuron as a random Gaussian process, the moments of which depends on both connectivity and activity in the network. For instance, for leaky integrate-and-fire neurons, this leads to the study of the Langevin-like equation

$$\tau_m \frac{dV}{dt} = -(V - V_L) + \bar{I}_{\text{syn}}(t) + \sigma \sqrt{\tau_m} \xi(t), \quad (6)$$

where $\bar{I}_{\text{syn}}$ represents the mean synaptic input and $\xi(t)$ a white noise term representing its fluctuations. In conditions in which correlations between these inputs can be neglected (as when the connection probability between cells is weak), a network of integrate-and-fire neurons can then be characterized by a Fokker–Planck equation that describes the time evolution of the instantaneous distribution of membrane potentials [1, 22, 105].

$$\tau_m \frac{\partial P}{\partial t} = \frac{\partial}{\partial V} [(V - \bar{I}_{\text{syn}}(t))P] + \frac{\sigma^2}{2} \frac{\partial^2 P}{\partial V^2}, \quad (7)$$

where the mean $\bar{I}_{\text{syn}}(t)$ is determined self-consistently from the neuron discharges.

In addition to the above mentioned analytical tools, numerical simulations are almost always indispensable, if only to check the validity of the approximations. While simulating rate models is relatively straightforward, simulations of networks of spiking neurons are, again, more demanding. In addition to standard finite-difference integration schemes [53, 57, 101], it is sometimes possible to use event-driven schemes, in which one jumps from one spike to the next, using an exact integration of network dynamics during inter-spike intervals (see [88]).

Intrinsic Network Dynamics

We start by a description of intrinsic network dynamics, that is, dynamics in absence of spatially or temporally structured inputs. In rate models, this means taking a constant and uniform input $I_{\text{ext}}(x, t) = I_{\text{ext}}$; in networks of spiking neurons, this means taking either a constant deterministic input, or a noisy stationary input. Noise is typically chosen to be a Gaussian random noise, uncorrelated from neuron to neuron, or uncorrelated Poisson processes independently activating all the neurons of the network.

The goal is then to understand the types of dynamics that can be generated by the network, independently of its inputs. Experimentally, intrinsic dynamics of a network can be observed in vitro, or in vivo, either in anesthetized animals or in awake animals in absence of specific inputs that activate the particular area under observation. Such experiments reveal many different types of activity that modelers have been trying to understand. A prominent and ubiquitous finding in in vivo recordings is irregular background activity at low rates. The issue of the origin and mechanisms of this activity can be addressed using networks of spiking neurons, and will be the topic of Subsect. “Irregular Firing at Low Rates”. We will then move to the issue of multistability in networks, which can be considered in the simple

setting of rate models. Finally, we will discuss the issue of synchronization and oscillations, which can be addressed both with rate models and spiking neuron models.

Irregular Firing at Low Rates

Recordings of cortical neurons *in vivo* show very irregular activity. The distributions of intervals between successive action potential emissions, commonly called inter spike intervals (ISI), are approximately Poissonian in a variety of cases. Understanding this irregularity, is a first theoretical challenge [15, 111]. Cortical cells receive on the order of 10^4 synapses. This large number should tend to promote regular firing since fluctuations of the total input should be small compared to its mean, unless inputs are strongly correlated. Another related difficulty is that measurements of synaptic weights [40, 56, 87, 110] (see [10] for a short survey) indicate that the detectable connections between pyramidal cells are relatively strong with a mean value of 0.5–1 mV, as measured from the peak somatic depolarization that they provoke. As a consequence, thousands of presynaptic pyramidal cells spiking at a low rate of a few Hertz should provide a strong depolarization of the post synaptic cells. It is thus not clear how a low rate of spike emission can be maintained in a recurrently coupled network. One loophole in the argument is that it does not take inhibition into account. Inhibition can potentially solve both puzzles at once when inhibitory inputs balance on average excitatory ones [6, 108, 120, 121]. This drastically reduces the input current so that low firing rates are possible. Moreover, current fluctuations can be comparable to the mean current, allowing for irregular firing.

These studies have shown that irregular firing is obtained in randomly connected networks of spiking neurons, as soon as recurrent inhibition is strong enough. Remarkably, such an irregular firing can be obtained even when the inputs to the network are deterministic, that is, in the absence of noise [120]. The nature of this irregular firing remains the subject of intense study. Irregular firing can be associated with complex but stable trajectories in phase space [63, 127], or with chaotic dynamics [127].

Recent data provide some evidence for a balance between inhibition and excitation in cortical

networks [109]. Somewhat unexpectedly, a balance of excitation and inhibition has also been found in the rhythmic input onto motor neurons during scratching behavior in turtles [13]. It is proposed that the associated enhanced irregularity can be used to produce a smoother muscle excitation.

Attractors with Inhomogeneously Distributed Activity

A recurring idea in theoretical studies is that structured connectivity can lead the dynamics of a given neural network to settle in one of several coexisting attractors with mean activity differently distributed among the different neurons of the networks. It is, for instance, central to Hop-field's view of memory storage in neural networks [58], as well as to proposed explanations for persistent activity underlying short-term memory.

Many designs of this type are based on short-range recurrent excitation together with long-range inhibition. The simplest embodies the so-called “winner-take-all” mechanism. It consists of two-recurrently coupled excitatory sub-networks inhibiting each other. This can be described in a rate model framework as

$$\tau \frac{dr_1}{dt} = -r_1 + \Phi(I_0 - Jr_2) \quad (8)$$

$$\tau \frac{dr_2}{dt} = -r_2 + \Phi(I_0 - Jr_1), \quad (9)$$

where r_1 and r_2 describe the activity of each sub-network and $J > 0$ the magnitude of recurrent inhibition. The homogeneous steady state has $r_1 = r_2 = r_s$ with

$$r_s = \Phi(I_0 - Jr_s). \quad (10)$$

However, linearization of Eqs. (8), (9) shows that homogeneously distributed activity is unstable when inhibition is sufficiently strong (the bifurcation itself can be supercritical or subcritical depending on the sign of the third derivative of Φ). In this case, the symmetry between the two neuronal populations is broken and there are two possible coexisting attractors with the activity enhanced in either sub-network enhanced and suppressed in the other one.

This scheme can be simply extended to several sub-networks (with global rather than reciprocal inhibition) to enlarge the possible number of coexisting attractors. Some neuronal networks, such as, for instance, the head-direction cell network, are thought to possess a line of attractors instead of a discrete set of attractors. This can again be obtained by generalizing Eqs. (8), (9) to cells labeled by a continuous parameter, which we denote by θ , with excitatory connections between cells with close values of θ and inhibition between cells with more distant values [5, 39, 48]. For illustrative purposes, we describe one such simple scheme proposed in [12], where for definiteness the continuous parameter is taken to correspond to an angle. This so-called ring model is a specific case of Eq. (5)

$$\begin{aligned} \tau \frac{d}{dt} r(\theta, t) &= -r(\theta, t) + \Phi \left[I_{\text{ext}} + \int_{-\pi}^{\pi} \frac{d\theta'}{2\pi} J(\theta - \theta') r(\theta', t) \right], \\ &\quad -\pi \leq \theta \leq \pi. \end{aligned} \quad (11)$$

It considerably simplifies the analysis [12] to restrict the synaptic coupling function to its first harmonic, $J = J_0 + J_1 \cos(\theta - \theta')$ and to take Φ to be a threshold linear f-I curve, $\Phi[I] = \beta[I]_+$ that is $\Phi[I] = \beta[I]$ for $I \geq T$ and 0 otherwise. Integration over θ reduces the dynamics to coupled differential equations for the first three moments r_0 , r_{11} and r_{12} of r with

$$\begin{aligned} r_0 &= \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} r(\theta), \\ r_{11} &= \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} r(\theta) \cos(\theta), \\ r_{12} &= \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} r(\theta) \sin(\theta). \end{aligned} \quad (12)$$

The homogeneous activity ($r(\theta) = r_0$) is non-zero for $I_{\text{ext}} > 0$, $r_0 = I_{\text{ext}}/(1 - \beta J_0)$; $\beta J_0 < 1$ is needed for the dynamics to be well-behaved that is, all-to-all interactions should be inhibitory, or at least not too excitatory, to prevent activity growth without bounds (or saturated activity when saturation is

included in Φ). However, homogeneous activity is unstable when interaction between cells with close values of θ is large enough that is, here for $\beta J_1 > 2$. Then, the network attractor is formed by a line of solutions in the form

$$r(\theta) = A[\cos(\theta - \theta_0) - \cos(\theta_c)]_+, \quad -\pi \leq \theta_0 \leq \pi. \quad (13)$$

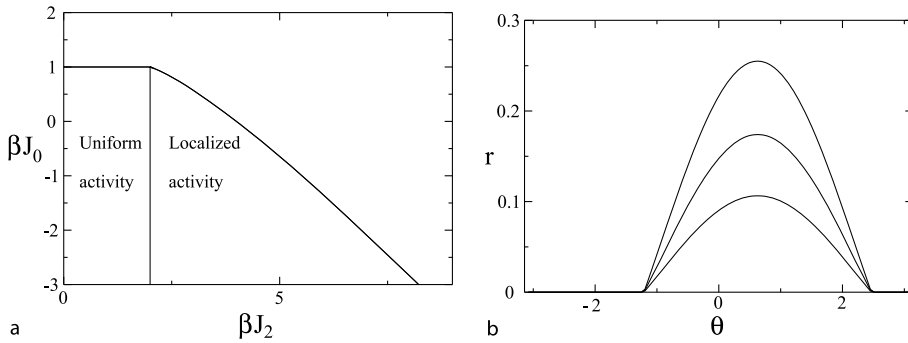
Thus, the network activity is confined to cells with parameter θ in a interval of values of width $2\theta_c$ around an arbitrary angle θ_0 . The constant θ_c , the solution selectivity, depends only on the magnitude of βJ_1 . Localized states of activity and their domain of existence in parameter space are shown in Fig. 4.

The ring model is a nice example of a model with a continuous line of attractors but it also exemplifies difficulties inherent to this type of models. The main problem is that a line of attractors is a fragile structure. It is not resistant to perturbations coming, for instance, from heterogeneity in the connection strengths or neurons' properties. If this design is used in real neural systems, there should exist additional mechanisms that maintain the line of attractors and avoid its breaking to a discrete set. Some proposals exist [70, 102], but the existence of a line attractor in an actual neural network remains to be demonstrated.

Dynamics at Various Time Scales

As has already been stressed, spontaneous activity in a variety of neural systems exhibits rhythmicity at time scales that range from a few millisecond to many seconds. We restrict ourselves to rhythms which are intrinsically of electrophysiological origins (unlike for instance, circadian rhythms which are accompanied by changes of neuronal excitability but which are thought to be primarily driven by changes in gene expression).

Bursts of Activity At the lower end of the spectrum, networks which produce repeated bursts of activities at a time scale of a few tenths of seconds to a few seconds are observed in different cases. They seem to be an essential component of



Neuronal Dynamics, Fig. 4 Ring model. (a) Phase diagram showing the position of the uniform and localized activity for the model of Eq. (11). (b) Profiles of localized

activity for $I_{\text{ext}} = 0.1$, $J_2 = 3$, and $J_0 = -2, -1, -5$ (from bottom to top). (Adapted from Ref. [12])

pacemakers generating locomotion [29] or respiration [69]. Repeated bursts of activity are also observed in neuron cultures [81, 93, 96]. An important additional example is given by the observation of up-down states in cortical slices [107], which are proposed to be analogous to slow oscillations during slow-wave sleep.

Specific models have been proposed for different systems but they appear to be based on the same general ideas. First, recurrent excitation allows for the self-sustaining bursting state. Second, this active state terminates when a slower building process has reached sufficient magnitude to prevent self-sustainment of the active state. The main contenders for the slow process are synaptic depression (see Subsect. “Dynamic Synapses”) or some intracellular mechanism such as a slow increase of an ionic concentration that opens an ion-gated channel once it has reached a threshold level. The generation of bursts of activity by synaptic depression has been modeled at a general theoretical level in [118]. In the context of respiratory rhythm generation, burst termination has been modeled as due to the slow inactivation of a Na^+ current (that is, termination of a depolarizing current) or by the activation of a calciumgated potassium (that is, hyperpolarizing) current. For up-down states, a sodium-dependent potassium conductance has been hypothesized to mediate their termination and has been taken into account in a proposed model [32]. The mechanism is illustrated in Fig. 5. Both calcium and sodium-gated potassium conductances have been

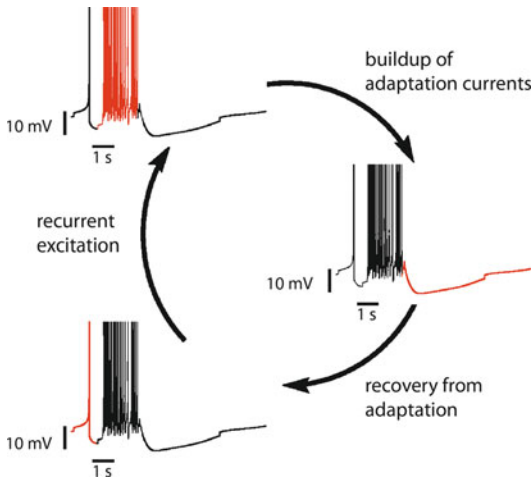
identified in spinal neurons [123]. It is worth noting however that in most cases the actual mechanism at work has not been experimentally pinpointed.

Besides burst termination, the cause of a burst should be determined to see how a repetition at about 1 Hz can come about. The general mechanisms appear again to be of two different types. Slow recovery from the termination process (for instance, return of concentration to a low level by the action of an ionic pump) can deterministically bring the networks above a threshold for excitation. Alternately, recovery can lead the network in a low activity state from which it can stochastically transit to the active state [126].

It is worth noting here that both the size distribution and duration distribution of bursts of activity in cortical slices have been examined using multi-electrode arrays [11]. Power law distributions corresponding to critical branching processes, reminiscent of a self-organized critical phenomenon [9], have been found. This was shown to emerge naturally from synaptic depression in a simplified IF neuron model without leak [77]. The applicability of this result to more physiologically realistic networks remains to be examined.

Wandering Between Different Attractors

Bursts of activity can be seen as a succession of jumps between two attractors with homogeneously distributed activity—a high activity state and a low activity state—mediated by a slow



Neuronal Dynamics, Fig. 5 Mechanism of slow oscillations in cortical slices. Recurrent excitation provokes a burst of activity which is terminated by a slow adaptation current. Activity resumes when the adaptation current has decayed. (From Ref. [32])

process. With structured connectivity, similar mechanisms can mediate transitions between a larger number of more complex coexisting attractors, as those described in Subject. “Attractors with Inhomogeneously Distributed Activity”. A given active state then consists of one particular subnetwork of active neurons among several possible ones. Some evidence for such stochastic visits of coexisting attractors has been provided both *in vitro* and *in vivo*. Using calcium imaging, mouse neocortical slices have been found to display sparse spontaneous activity and sets of coactive neurons that repeatedly appear above chance level [33]. *In vivo*, neurons of cat visual cortex responding to the same preferred orientation (the so-called orientation maps) have also been reported to be spontaneously coactive, with sets belonging to different orientations appearing in time in a stochastic manner [67, 115]. A model with biologically plausible connectivity and attractors consisting of orientation maps is able to reproduce these remarkable data [17]. It should be noted, however, that the experimental results seem also to be interpretable as fluctuations about a single background state driven by correlated thalamic inputs [49].

Interestingly, a similar set of ideas has been used to model slow oscillations in higher

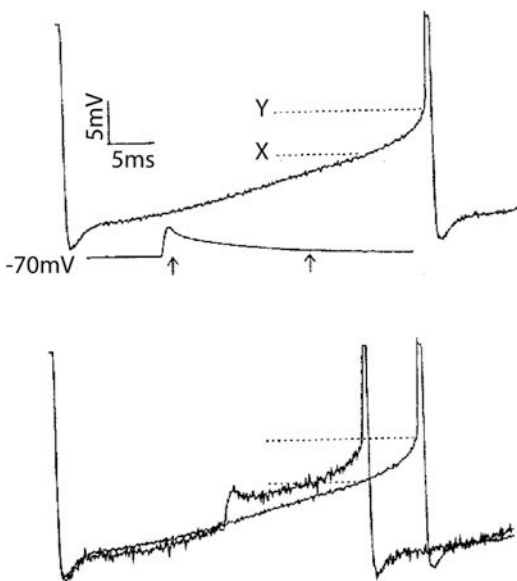
cognitive tasks. One interesting example is binocular rivalry: when the right and left eyes are presented with two different images, the perceived pattern alternates between the two images every few seconds. Moreover, several functional magnetic resonance imaging studies have shown that fluctuation in neural activity in several brain areas correlates with perception changes [80, 100, 114]. The dominance of the perception of one image over the other one has been modeled as a competition between two recurrently coupled excitatory networks reciprocally inhibiting each other, the “winner-take-all” design described in Subject. “Attractors with Inhomogeneously Distributed Activity”. Without further elaboration this gives rise to two attractors: either one of the two networks can be active with the other silenced. Similarly to burst or upstate termination, alternation between attractors (and percepts) can arise by supplementing this basic design with a slow process. It has been modeled either as coming in a deterministic way from synaptic depression [124] or from a stochastic jump from one of the two attractors to the other [92].

Synchronization of Periodically Firing Neurons

Neural recordings show oscillations in diverse frequency bands. They depend both on the neural structure and, when recorded *in vivo*, on the type of activity that the animal is performing. These rhythms, which are seen in EEG or local field potential, emerge from the coordinated activity of many neurons. Synchronization of nonlinear oscillators [99] has of course been thoroughly studied since its discovery by Huyghens. Some of the tools developed [73] have been directly applied to neurons in a regime where they emit action potentials in a periodic manner [52, 122]. Many experimental and theoretical studies have focused on single neurons and coupled pairs of neurons to infer synchronization properties of large networks of weakly coupled neurons. This has acquired renewed importance with the discovery that inhibitory interneurons in the same subtype category appear to be preferentially coupled [45, 47]. For weak coupling, the dynamics of an oscillator can be described by the behavior of its phase, that is, its position

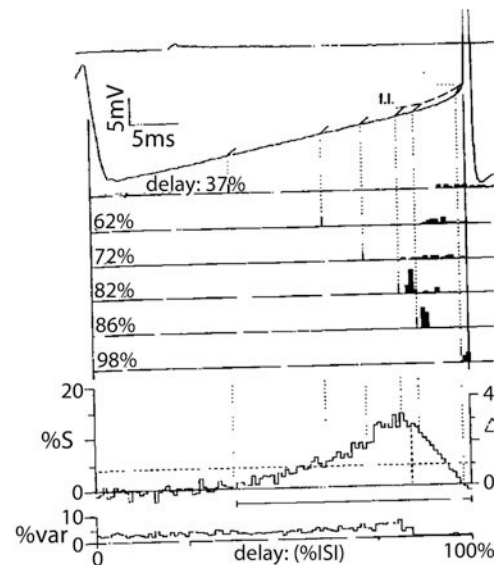
along its limit cycle. How the spike advance/delay produced by a short current injection depends on the time of injection during the interspike interval is a crucial quantity for synchronization. This so-called phase-response-curve (PRC) has been studied in different models [52, 122] with the result that generally a small and short depolarization advances the next spike, and does so to a greater extent the more closely it occurs before spike emission. This is referred to as a type I PRC. In some cases, though, (as in the original Hodgkin- Huxley model) a less intuitive type II PRC is found: a small depolarization just after the spike has a greater effect on hyperpolarizing currents than on depolarizing ones and results in a delay of the next spike. The PRC has also been experimentally measured for neocortical neurons. The results of the early experiment of [103] are shown in Fig. 6 and give a type I PRC. For instantaneous synaptic transmission, this would lead one to expect that excitatory interactions tend to make two identical neurons spike in

phase while inhibitory ones would push them to antiphase spiking. It was therefore an important theoretical finding that, for more realistic synaptic currents with finite rise and decay, this is not generally the case and that inhibition can be more efficient than excitation for synchronization. For excitatory synapses, complete in-phase spiking is generally unstable for type I PRC and a finite dephasing exists even for identical neurons. On the contrary for inhibitory synapses, in-phase and anti-phase spiking are both possible at low frequency, a bistable situation. However the attraction basin of the in-phase state grows with frequency, and above a threshold frequency the anti-phase state disappears. This leads one to expect a transition from antiphase to in-phase spiking for a coupled pair of identical interneurons as their firing frequency increases. This has been verified experimentally [46] as well as other similar predictions for gap junctions or on the combined effect of inhibitory synapses and gap junctions [31, 78, 84].



a

Neuronal Dynamics, Fig. 6 Measurement of phase-response curve (PRC) for neocortical neurons [103]. The authors injected a short depolarizing current pulse at different times during the interspike interval. As shown on the *left panel*, this results in a timing change for the spike following the current injection. The *right panel* show



b

results for different injection times as well as the PRC which summarizes the data by giving the spike time changes as function of the current injection time (expressed here as a percentage of the ISI). (Adapted from Ref. [103])

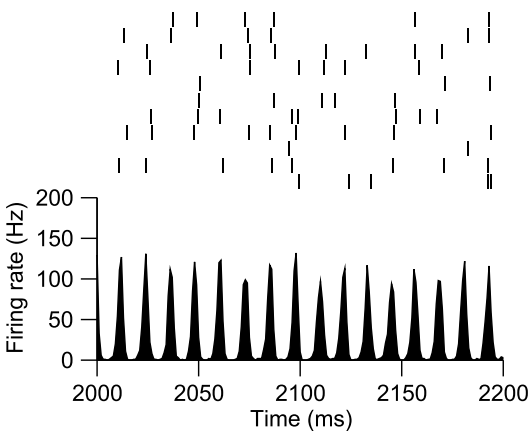
Sparsely Synchronized Oscillations Although a substantial amount of work has been devoted to analyzing periodically firing neurons with a minimal amount of noise and heterogeneity, this seems to be a rather infrequent situation in the brain. Strong heterogeneity appears to be the norm rather than the exception. Moreover, as explained in Subsect. “Irregular Firing at Low Rates,” the activity of most neurons appears quite irregular and their discharge rate is often low compared to the frequency of gamma oscillations and faster rhythms. This is also the case in vitro when pharmacologically-induced activity in hippocampal slices results in spontaneous gamma oscillations [41]. Modeling studies have shown that a mechanism distinct from the Huyghens-type synchronization of oscillators can produce a fast and robust rhythm at the network level with neurons discharging irregularly and at a lower frequency [23]. An example from a simulation of a network of IF neurons is shown in Fig. 7. Recurrent inhibition again plays an important role in these sparsely synchronized oscillations. The basic idea can

be understood from a rate model description similar to Eq. (1)

$$\tau \frac{dr}{dt} = -r + \Phi[I_{\text{ext}} + Jr(t - D)], \quad (14)$$

where the activity $r(t)$ of the network at time t is influenced by its activity at a previous time $t - D$. The delay D models in a crude but effective way the latency and finite kinetics of synaptic currents (see Eq. (4)). It is not difficult to show that for $J < J_c < 0$, that is, for a sufficiently strong recurrent inhibition, the activity $r(t)$ is attracted to a limit cycle and oscillates periodically. The oscillation frequency is of order $1/D$ and increases from $f = 1/(4D)$ for delays short compared to τ to $f = 1/(2D)$ for delays long compared to τ . It is simple to see the origin of the oscillations: an increase of activity in the network at time t provokes an increase of recurrent inhibition. This results in a decrease in network activity at about $t + D$, since transmission from one neuron to the next takes a time D . This decrease of activity at $t + D$ itself again generates an increase of activity at about $t + 2D$ from which the cycle can continue. One sees that the frequency of the network oscillation, of order $1/D$, is directly linked to the kinetics of synaptic transmission but not related to the neuron discharge rate r . While the rate description of Eq. (14) simply captures some characteristics of network oscillations in the sparsely synchronized regimes, it is far from providing accurate estimates, in particular for the oscillation threshold. A more complex mathematical description based on the Fokker–Planck equation has been developed to this end [22, 25]. It allows, moreover, the inclusion of various features of single neuron dynamics such as the finite rise time of the action potential [42] or of an eventual resonance in subthreshold dynamics [26, 104] (see [23] for a short review).

Although many experimental recordings are suggestive of this kind of oscillations in the brain, it is not easy to eliminate the possibility that the observed rhythm is created by a population of fast-spiking unidentified cells. At present, two of the best studied examples are provided by fast oscillations in the hippocampus and the



Neuronal Dynamics, Fig. 7 Oscillations with sparsely firing neurons in a fully connected network of 1000 leaky integrate-and-fire neurons receiving independent white noise sources. The *top panel* shows a raster of 10 neurons, while the *bottom panel* shows the network instantaneous firing rate (computed in 1 ms bins). The network oscillates at about 90 Hz, while single cells fire at about 30 Hz, as predicted by theory [22, 25] (synaptic time constants: 1 ms latency, 1 ms rise time, 6 ms decay time). (Reproduced from Ref. [21])

cerebellum. The “ultrafast” ripple oscillations (140–200 Hz) are the fastest among the numerous hippocampal rhythms. They occur together with “sharp waves” during awake immobility and slow wave sleep in rats. Recordings show that both the discharge rates of pyramidal cells and interneurons (average rates 8 Hz and 30 Hz respectively [34]) are much lower than the frequency of the population oscillation. In the cerebellum, fast oscillations were discovered by Adrian in one of the first intracranial recordings [3]. More recently, de Solages et al. [37] have provided strong evidence that these fast (150–250 Hz) oscillations are emerging from recurrent inhibition among Purkinje cells that themselves fire at an average of about 40 Hz.

Wave Propagation The propagation of waves of neural activity is certainly an important topic but one that has traditionally been difficult to study experimentally. It has therefore been the subject of relatively few specific theoretical works. Wave propagation in neural networks has been classically analyzed in the framework of rate models [5, 39] with results for wave existence similar to those for general excitable media (for which many studies exist motivated, for instance, by applications to chemical waves in the Belousov–Zhabotinsky reaction or, in a biological context, to electrical waves in cardiac tissue). Advances in imaging techniques are now providing more data on neural activity propagation, in slices [18, 72, 107], in cell cultures [62] and even in vivo [98]. In parallel, theoretical interest in spiking models is developing and results have been obtained either by the analysis of simplified cases [50] or by simulations [32]. The results highlight in particular the role played by inhibition and the potential importance of long-range connections in wave propagation.

Stimulus Driven Dynamics

What happens when external stimuli are presented to a network of neurons? An external stimulus is usually modeled as an increase (or decrease) of external inputs to specific groups of neurons. For

example, in the ring model, presentation of an external stimulus representing an oriented bar during an interval $[0, T]$ is described by $I_{\text{ext}}(\theta, t) = I_0 + I_1 \cos(\theta - \theta_s)\Theta(t)\Theta(T - t)$, where θ_s is the angle of the presented bar. In a spiking neuron model, an external stimulus can be represented by a transient change of the mean currents impinging on a subset of neurons, or by a transient change in the frequency of incoming spike trains. Conceptually, these transient inputs can lead to three types of phenomena: (i) During the transient input, the nature of the dynamics of the network can change qualitatively. For example, the network might switch from an asynchronous to a synchronous state or it might switch from a uniform to a spatially localized state. (ii) In multistable networks, the stimulus can switch the network from one state to another, and the network will then stay in this particular state, thereby maintaining a short-term memory of the stimulus that was presented. (iii) Presentation of a stimulus can induce synaptic plasticity between neurons that are activated/inactivated by the stimulus, leading to a remodeling of the network, and therefore potentially to a change in the repertoire of states that the network dynamics can sustain. We now briefly examine these three phenomena before focusing on specific systems.

Dynamics During Stimulus Presentation

Selective Amplification The simplest change induced by external stimuli is a change in firing rates of the neurons. This change in rate is governed by external inputs, but also by recurrent connectivity. This can be best studied in the context of rate models (see [35]). In general, excitatory networks tend to amplify external inputs, while inhibitory networks tend to attenuate them. With spatially structured connectivity, the network will tend to amplify certain inputs, at the same time attenuating another. A typical example is represented by the ring model of Subsect. “Attractors with Inhomogeneously Distributed Activity” with a ‘Mexican-hat’ connectivity – with this type of connectivity (excitatory at short-range, inhibitory at long-range), the network tends to amplify spatially localized inputs, while it will attenuate inputs with no spatial selectivity.

Thus, the network has the property of selective amplification. When the excitatory connectivity is strong enough and one enters the marginal phase, the network generates spatially localized states even in absence of external inputs. In this case, the external stimulus selects one of the possible network states (a state in which the activity is peaked around the most strongly activated neuron) out of the repertoire of possible states (a continuum in the case of the ring model). This property is consistent with several experimental findings in various areas [67, 79].

Switching from Asynchronous to Synchronous State

Another effect of external stimuli can be to change the degree of synchrony in the network. For example, a stimulus can switch a network from an asynchronous state to a synchronous state (or vice versa). This is typically what happens in randomly connected networks of excitatory and inhibitory neurons (or purely inhibitory networks) when inhibition is stronger than excitation [20, 22]. This is due to the fact that external inputs tend to increase the average firing rate of the network, leading to an effective increase in the strength of inhibitory feedback. This increase can potentially make the network switch from the asynchronous to the synchronous region.

This emergence of synchronous activity induced by external inputs is reminiscent of many experimental findings, from oscillations induced by odors in the olfactory system (to be discussed in more detail below), to oscillations correlated with selective visual attention in the visual system of the primate [44]. The emergence of oscillations in the presence of visual inputs has also been hypothesized to allow the system to solve the so-called ‘binding problem,’ though this issue remains hotly debated [59, 71, 106].

Multistability and Working Memory

In multistable networks, stimuli can potentially switch the network from one state to another. For example, in winner-take-all rate models, a stimulus will switch the network to an attractor state in which the population that received the largest input is active, while all others are inactive. The

fact that this network configuration is an attractor means that the network maintains, in short-term memory, some information about which stimulus it was shown. This property is the hallmark of associative memory models, where many ‘memory states’ in which subpopulations of neurons are selectively active at higher rates, are attractors of the network dynamics, thanks to strong excitatory feedback inside such sub-populations. It is widely believed to form the basic mechanism underlying working memory, that is, the active maintenance of information in short-term memory. Such networks have been investigated extensively in the last three decades, from networks of simplified binary neurons [58] to networks of spiking neurons of increasing realism see [6, 24]). The working of such a network is illustrated in Fig. 8.

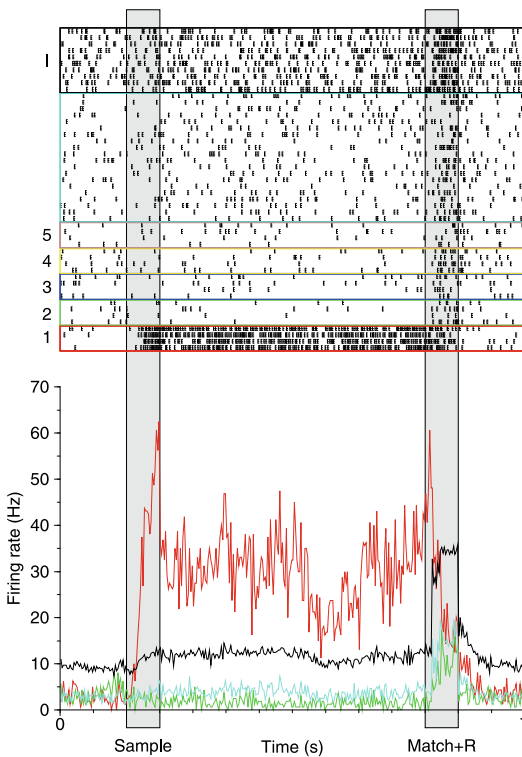
Effect of Long-Term Synaptic Plasticity on Network Dynamics

Another potential effect of external stimuli is to modify the synaptic structure of the network. For example, in associative memory models, external stimuli are assumed to lead to synaptic modifications induced by increases or decreases of firing rates of single neurons. Hebbian learning rules posit that synapses connecting two neurons which are strongly activated by the same stimulus will potentiate, while synapses connecting one strongly activated neuron to an inactivated neuron will depress. This learning dynamic tends to create a synaptic structure that leads to attractors strongly correlated with the state of the network during stimulus presentation.

Most network studies have separated neuronal and synaptic dynamics, assuming much slower synaptic dynamics. Typically, one studies the network with a fixed synaptic structure that incorporates, in a Hebbian way, learning of patterns of activity presented to the network in the past. More recently, there have been studies of networks with double dynamics of neurons and synapses [60, 91].

Dynamics and Information Processing: Two Specific Examples

In some neural structures, the role of dynamics in information processing has been particularly



Neuronal Dynamics, Fig. 8 Dynamics of a randomly connected network of excitatory and inhibitory neurons with working memory properties (*top*: raster; *bottom*: average firing rate of different populations of neurons). Inhibition is strong enough to stabilize the network in a background state (before ‘sample’ presentation). External stimuli have been ‘stored’ in the synaptic matrix, through enhanced synaptic connectivity between neurons that belong to a subpopulation that is activated by a stimulus (sub-populations 1–5 in the figure). Presentation of an external stimulus (sample 1 in the figure) increases the firing rate of the relevant neurons (see *red curve* in *bottom panel*, average firing rate of neurons in population 1). This enhanced firing rate survives removal of the stimulus because of the strong excitatory connectivity between 1 neurons. Hence, the stimulus has switched the network from the background state to the memory state corresponding to stimulus 1. Finally, a sufficiently strong non-specific stimulus switches the network back to the background state. (From Ref. [24])

scrutinized. We briefly describe here two prominent cases and some views and hypotheses that they have suggested.

Dynamics and Odor Discrimination As recalled previously, it has been known since the recordings of Adrian [4] that odors promote

gamma oscillations in the olfactory bulb. The role of oscillations in odor processing has, however, remained unclear in spite of interesting proposals [43]. Olfaction is an evolutionarily ancient function and the associated neural structure are analogous in very different species. Recent recordings in insects are shedding new light on the role of dynamics in odor discrimination. The antennal lobe in insects corresponds to the olfactory bulb in mammals. It receives input from neurons in the olfactory epithelium and its principal neurons project to the next structure, the “mushroom body”. In the locust, puffs of two close odors induce antennal lobe activities that are similar at start (as measured from the activity of a sample of the eight hundred projection neurons) but that diverge in a few hundred milliseconds [113]. The antennal lobe oscillations shape its output as successive volleys of projection neuron spikes emitted at a rate of about 20–30 Hz. The numerous Kenyon cells in the mushroom body then appear to function as coincidence detectors that process each projection neuron spike volley independently of the others [89, 113] (reset between each volley being provided by non-specific feedforward inhibition coming from lateral horn interneurons [97]). The precise timing of the whole process appears to allow STDP plasticity at the Kenyon cells output synapses [30] and presumably memory formation in a way that remains to be related to behavioral experiments and genetic data [54, 66].

Place Maps and Oscillations in the Hippocampus The hippocampus is another brain region in which oscillations are prominent and one in which their role in information processing is among the best studied. The hippocampus is an important structure for navigation. “Place” cells that fire at particular locations have been discovered 30 years ago in the rat hippocampus [94]. Different place cells discharge in different “place fields”, of about 25 cm in size, and recording several cells allows the determination of the animal position in its environment. However, place cell firing is also strongly modulated at theta frequency. The phase of a place cell discharge advances as the animal enters the place

cell field [95]. So, monitoring precise spike timing with respect to the theta oscillations provides supplementary information and a more accurate position determination [64, 125]. Several models have been proposed for place cell formation during exploration of a new environment, some based on network dynamics [116] related to that exposed in Subsect. “Attractors with Inhomogeneously Distributed Activity”, other based on temporal modulation of single cell spiking created by addition of oscillations at different frequencies [65, 76, 95]. Supplementary complexity and theoretical puzzle has been added by the startling discovery of “grid” cells [51, 90] in the entorhinal cortex, a neural area in the hippocampal formation by which transits much of the sensory information that reaches the hippocampus.

Future Directions

We are still far from having a precise understanding of how neural systems operate, but there are daily advances at all levels from the description of detailed molecular mechanisms to that of high-level cognitive processes. We limit ourselves here to underlining some areas where further investigations of dynamics are clearly needed.

We have focused on networks with very little spatial structure but propagation and spatio-temporal dynamics most surely play important roles in neural information processing. This appears to be a very rich domain that imaging and theoretical investigations will help to explore.

A related question is that of the coordination between different neural areas. How do dynamics in one structure, for instance oscillations, serve to transmit and process information in a connected structure? As mentioned above, recent investigations of olfaction in insects provide a fascinating glimpse on this question. It will clearly be necessary to address it more generally in spite of the experimental difficulties.

Our emphasis in this article has been on electrical activity and its transmission. Another all-important aspect is neuromodulation which affects neuron properties on a slower time scale and probably a less local spatial scale. At present,

the relation between these two facets of neural activity has been considered in few theoretical studies, but this needs to be thoroughly addressed in future work.

Homeostasis, or how dynamical properties of neuronal networks are maintained, is another question that needs analysis. Interesting experimental and theoretical work has been performed using the stomatogastric of the lobster as an example [75, 85], but certainly this important topic requires further scrutiny.

These few questions among many others should make it clear that investigation of neuronal dynamics requires the development of powerful experimental techniques and theoretical analyses and that the subject will remain a topic of intense research in the forthcoming years.

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Dense Active Matter

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Article Outline

Glossary

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Properties of dense systems of active objects with self-propulsion are reviewed with emphasis on glassy behavior and jamming. Experimental realizations of such systems are pointed out, and the effects of the presence of self-propulsion forces on the properties of passive glass-forming liquids are discussed, with special attention to the dependence of the observed behavior on the strength and persistence time of the self-propulsion force. Results obtained from theoretical and numerical studies of simple models of dense active systems are summarized and compared with the results of experimental studies.

Glossary

Active matter Collection of objects with self-propulsion forces.

Cytoplasm Viscous fluid that fills the inside of a cell.

Epithelial sheet Single layer of cells with every cell in direct contact with the membrane that separates it from the underlying connective tissue.

Fragility A parameter that quantifies the rate of growth of the viscosity of a liquid with decreasing temperature or increasing density.

Glass Disordered solid obtained by rapidly cooling or compressing a liquid.

Persistence time Timescale of decorrelation of the direction of the self-propulsion force.

Strength of activity Magnitude of typical self-propulsion force.

Why Study Active Matter?

Active matter consists of objects that can convert internal or ambient sources of energy into systematic motion (Schweitzer 2003). It includes any nonequilibrium condensed matter system, whether it is composed of living or nonliving matter, in which “self-propulsion” forces are present. Experimentally studied active matter includes living systems such as flocks of birds (Cavagna and Giardina 2014), schools of fish (Katz et al. 2011), swimming bacteria (Wolgemuth 2008; Peruani et al. 2012), migrating cells, (Angelini et al. 2011) and molecular motors (Kodera et al. 2010), as well as synthetic nonliving examples such as vibrated granular matter (Kumar et al. 2014), self-propelled colloids (Jiang et al. 2010; Buttinoni et al. 2013), magnetic nano-propellers (Ghosh and Fischer 2009), Quincke rollers (Bricard et al. 2013, 2015), and swimming microrobots (Peyer et al. 2013). Since active systems are characterized by self-propulsion forces that do not arise from interparticle interactions, they are outside thermodynamic equilibrium (Ramaswamy 2010; Marchetti et al. 2013). These systems have received a lot of attention in recent years because they exhibit novel collective behavior (Ramaswamy 2010; Marchetti et al. 2013; Bechinger et al. 2016), such as flocking

(Toner and Tu 1998), giant number fluctuation (Ramaswamy 2010), motility induced phase separation (Cates and Tailleur 2015), and active turbulence (Thampi and Yeomans 2016).

Definition of the Subject

In this entry, we consider dense active systems that exhibit glassy behavior or jamming (Janssen 2019; Berthier et al. 2017). When a liquid is cooled sufficiently fast so that crystallization is avoided, it enters a supercooled liquid state which, upon further cooling, undergoes a transition to an amorphous solid state that is called a glass (Binder and Kob 2011). A similar phenomenology is found when a system of hard particles is compressed sufficiently fast. The supercooled liquid state near the glass transition exhibits many interesting properties (Berthier and Biroli 2011), the most remarkable among these being a rapid growth of the viscosity and the structural relaxation time with decreasing temperature or increasing density. This growth is faster than Arrhenius in “fragile” liquids and follows the Arrhenius form in “strong” liquids (Angell 1995). Jamming, on the other hand, refers to a purely geometrical process in which the freedom of movement of the constituting particles is lost. When a system of particles without thermal fluctuations is compressed from a low density, it undergoes a jamming transition (Liu and Nagel 2010) at which macroscopic rigidity sets in. We focus on how the behavior of dense systems near the glass or jamming transition is modified by the presence of activity. Aligning interactions that may induce flocking behavior (Cavagna and Giardina 2014) are not considered and hydrodynamic interactions between active particles are neglected.

Experimental Studies

Glassy dynamics has been observed in a variety of active biological systems. Several experimental studies (Zhou et al. 2009; Nishizawa et al. 2017; Parry et al. 2014) have revealed the occurrence of glassy dynamics in the cytoplasm of cells. These

studies show a transition from a fluid state to a glass as the strength of activity is reduced. Activity is also found to decrease the fragility (Angell 1995) of the liquid state. Similar results have been obtained in a study of the dynamics of micron-size particles embedded in cell nuclei (Hameed et al. 2012).

Another class of dense active systems that has received a lot of experimental attention consists of two-dimensional epithelial sheets and three-dimensional assemblies of cells. Angelini et al. (2011) have presented evidence for fragile glass-like behavior in confluent epithelial monolayers of Madin-Darby Canine Kidney (MDCK) cells. Garcia et al. (Garcia et al. 2015) have found evidence for a jamming transition in a monolayer of human bronchial epithelial cells. Recently, Henkes et al. (2020) have shown that displacement and velocity correlations in epithelial monolayers are reminiscent of those in supercooled liquids. A connection between a liquid-to-glass transition in layers of human bronchial epithelial cells and the occurrence of asthma has been demonstrated in the work of Park et al. (2015). Signatures of glassy dynamics have also been observed in three-dimensional collections of cells in embryogenesis (Schötz et al. 2013), wound healing (Vishwakarma et al. 2020), and metastasis of cancer (Palamidessi et al. 2019).

A recent study (Klongvessa et al. 2019a, b) of glass transition in synthetic active matter has considered two-dimensional layers of Janus colloids (gold particles half-coated with platinum) in which self-propulsion forces are controlled by the concentration of hydrogen peroxide. The main result of this study is the observation that the relaxation time decreases with increasing activity if the packing fraction is not very large. On the other hand, if the packing fraction is very large, such that the dynamics is nonergodic in the absence of activity, then the introduction of activity is found to slow down the dynamics. This slowing down is followed by fluidization at higher activity.

Models

Theoretical and numerical studies of dense active systems have been carried out mostly for particle-

based models. The simplest particle-based model, known in the literature as Active Brownian Particles (ABPs) (Romanczuk et al. 2012), consists of particles with spherically symmetric interactions. Activity in the system is modeled by a random self-propulsion force with magnitude f and persistence time τ_p that describes the timescale of decorrelation of its direction. The overdamped equations of motion of the constituent particles in the ABP model in two dimensions are given by

$$\gamma \dot{\mathbf{x}}_i = \sum_{j \neq i} \mathbf{f}_{ij} + f \mathbf{n}_i + \mathbf{y}_i, \quad (1)$$

$$\dot{\theta}_i = \zeta_i,$$

where γ is a friction coefficient, $\mathbf{f}_{ij}$ is the force exerted on particle i by particle j , $f \mathbf{n}_i$ is the self-propulsion force, and $\mathbf{y}_i$ is a thermal noise with zero mean and variance $2k_B T \gamma \delta(t-t_0)$ that obeys the fluctuation-dissipation relation (T is the temperature and k_B is the Boltzmann constant). The direction $\mathbf{n}_i \equiv (\cos \theta_i, \sin \theta_i)$ of the stochastic self-propulsion force undergoes rotational diffusion described by the noise ζ_i with zero mean and correlation $\langle \zeta_i(t) \zeta_j(t') \rangle = 2\tau_p^{-1} \delta_{ij} \delta(t-t')$. Its effect on the $\mathbf{x}_i$ -dynamics is that of an exponentially correlated vectorial noise with correlation time τ_p . In Brownian dynamics simulations, these equations of motion are numerically integrated forward in time. In simulations of glassy behavior, one typically considers binary mixtures or poly-disperse systems in order to avoid crystallization. Models of active rod-like particles, such as dumbbells, have also been considered in simulations (Mandal et al. 2017). The self-propulsion force in such models is usually assumed to have a fixed magnitude f , and to act along the long axis of each rod-like particle. The persistence time of the active force is not an independent variable in these models – it is determined by system parameters such as the density, the temperature, and the strength f of the active force.

Studies of the collective dynamics of living cells in tissues involve a different class of models. These models are different from the particle-based models described above in that the cells in these models cover the entire space without any gap

between neighboring cells. In vertex models (Bi et al. 2015; Barton et al. 2017) of confluent layers of epithelial cells, the cells are represented as polygons that share edges. The energy of a collection of cells is defined in terms of the areas and perimeters of these polygons. Activity is incorporated in the model by the addition of a velocity of fixed magnitude and random direction in the equation of motion of the cells. Variants of the vortex model include the Voronoi model (Bi et al. 2016) and the cellular Potts model (Chiang and Marenduzzo 2016).

Numerical Studies

Similar to other domains in soft matter, computer simulations have been very useful to study structural and dynamical behavior of active matter systems. The standard procedure has been to consider conventional models of passive liquids whose phase behavior has been extensively characterized and introduce activity in these model systems to study how the known properties get modified. One of the first numerical studies (Ni et al. 2013) involved probing the effects of activity on the slow dynamics of a three-dimensional hard sphere system. A similar study (Berthier 2014) was carried out at about the same time for a two-dimensional system of hard disks. In both cases, it was observed that with increasing activity, the relaxation timescale decreases, at any packing fraction, which consequently pushes the glass transition density to higher values.

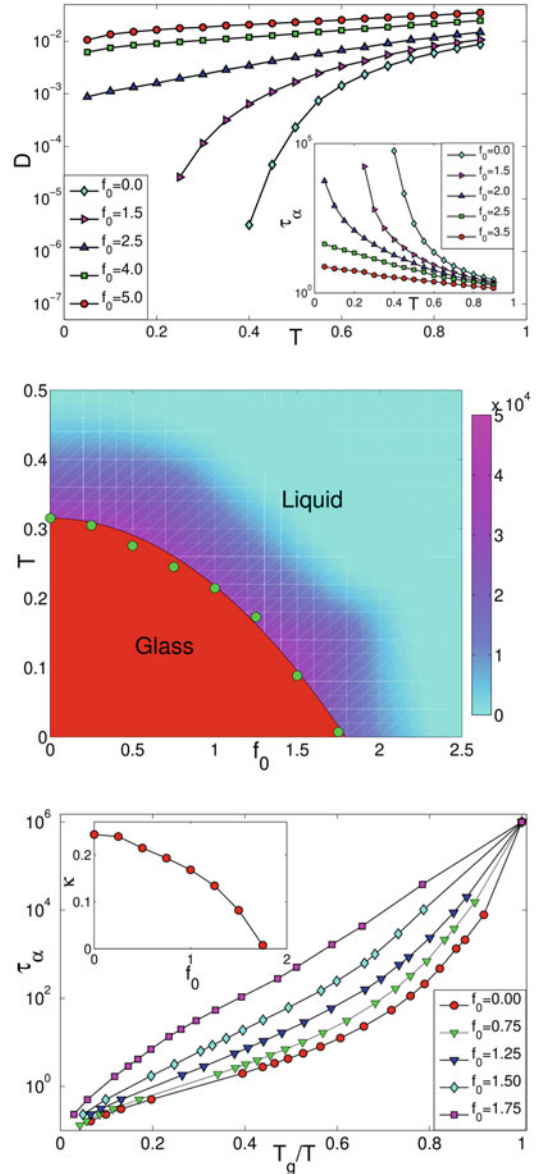
The effects of including activity in a well-studied model glass former, viz. the Kob-Andersen binary Lennard-Jones mixture (Kob and Andersen 1994), were studied in Ref. (Mandal et al. 2016) wherein active forces were assumed to be present for one of the constituent species. The active particles were randomly assigned self-propulsion forces of fixed magnitude f_0 , chosen such that there is conservation of the net momentum of the system. After a persistence time τ_p the directions of the active forces were randomized, while maintaining momentum conservation. The dynamical properties of this system at different temperatures were probed via

the mean-square-displacement (MSD) of tagged particles, $\langle |\Delta \mathbf{r}(t)|^2 \rangle$, and the self-overlap function, $Q(t)$. Relatively small values of τ_p were considered in this study.

In the absence of activity, the glass-forming mixture is a liquid at high temperatures. With the lowering of temperature, the diffusion coefficient, D , extracted from the MSD decreases, along with the increase in the relaxation timescale, τ_α , extracted from the decay of $Q(t)$. A glass transition temperature for the system can be estimated by fitting τ_α to the well-known Vogel-Fulcher-Tammann (VFT) form, $\tau_\alpha = \tau_\infty \exp \{1/(\kappa(T/T_{\text{VFT}}-1))\}$, where κ is the kinetic fragility, τ_∞ is the relaxation time at high temperatures, and T_{VFT} is identified as the putative glass transition temperature.

In the presence of active forcing, the dynamics gets accelerated and the temperature dependence of the diffusion coefficient becomes weaker. This is illustrated in the top panel of Fig. 1 where the temperature dependence of the long-time diffusion coefficient D has been shown for different values of f_0 . Similarly, the temperature dependence of the relaxation timescales, τ_α , shows a weaker increase with decreasing temperature as f_0 is increased. The phase diagram in the middle panel of Fig. 1 shows the values of T_{VFT} for different values of f_0 , as extracted via VFT fits of the data for the relaxation time τ_α . It shows that even in the presence of finite activity, there is a thermal threshold below which the glassy regime is obtained. However, this threshold vanishes at high enough active forcing. This is qualitatively different from the behavior found in Refs (Berthier 2014). and (Ni et al. 2013) in which a (putative) glass transition was found to be present for all finite values of the strength of the activity. This important observation tells us that some of the effects of activity on the glass transition are sensitive to the nature of the system (whether controlled by temperature or density) and the details of the self-propulsion mechanism.

Another interesting observation regarding the effect of activity on glassy dynamics is the decrease of kinetic fragility of the liquid with increasing activity. This is illustrated via the so-called ‘‘Angell plots,’’ shown in the bottom panel of Fig. 1, where one plots τ_α vs T_g/T , T_g



Dense Active Matter, Fig. 1 Effect of activity on a three-dimensional glass-forming liquid (Kob-Andersen binary Lennard-Jones mixture) (Adapted from Ref. Mandal et al. 2016). (Top) Diffusion coefficient (D) vs temperature (T) for $\tau_p = 4.0$ and different active forcing (f_0), as marked. The inset shows the corresponding relaxation timescales, τ_α . (Middle) Phase diagram in the T - f_0 plane. The color indicates the value of τ_α according to the colorbar. (Bottom) Angell plot, showing variation of τ_α with T_g/T for different f_0

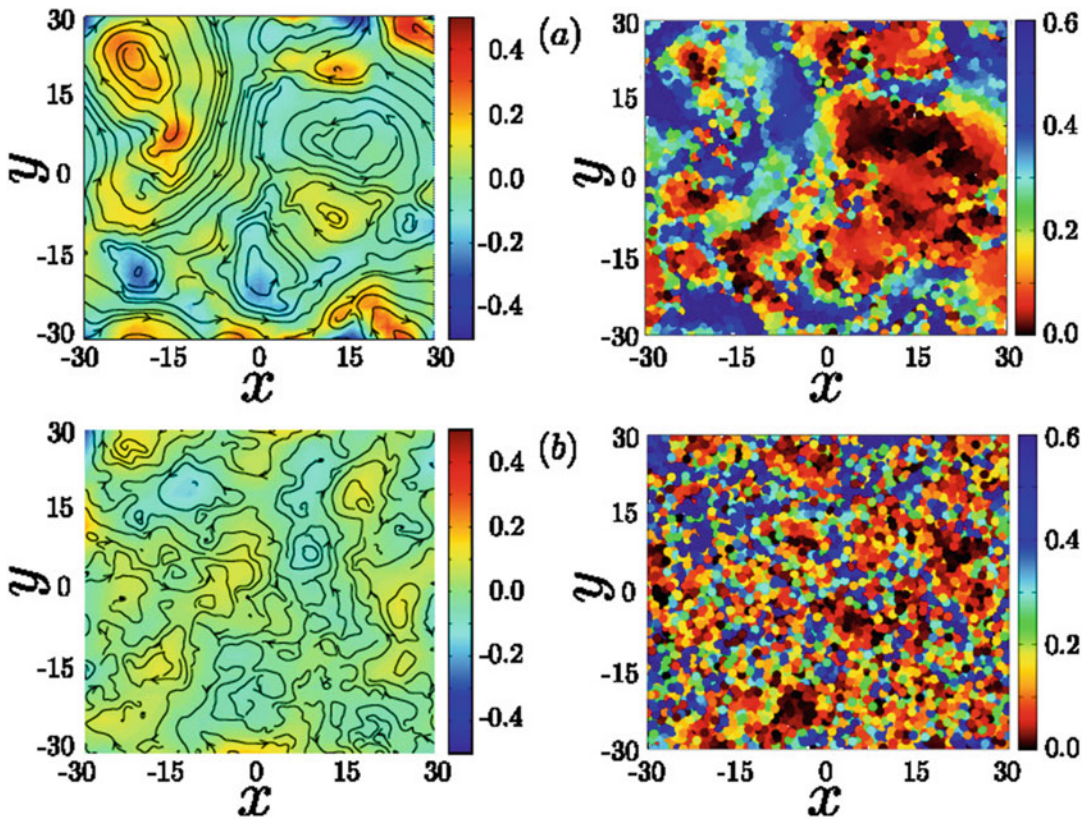
being the analog of the experimentally determined glass transition temperature at which the viscosity is 10^{13} poise, obtained from the definition τ_α

(T_g) = 10^6 . The curvature of the plots gives us a measure of the fragility, κ , which is seen to decrease with increased forcing as shown in the inset of the bottom panel of Fig. 1.

The question of whether the dynamics in passive and active supercooled liquids are different was investigated in Ref. (Mandal et al. 2017) using a two-dimensional dense assembly of self-propelled dumbbells. Specifically, maps of the displacement field of the center of mass of the dumbbells were computed for state points in the $(T-f_0)$ plane having similar relaxation timescales. In the passive limit, these maps do not reveal any spatial structures or correlations. As one increases the strength of the activity along the iso-relaxation time line, vortex-like structures become visible (see Fig. 2) and the size of these

vortices increases with increasing activity. Further, the displacement maps, constructed over the structural relaxation timescales, show that the active system exhibits more dynamical heterogeneity than the passive one. The correlation lengths associated with these spatial structures increase as one moves along the path of iso-relaxation timescales in the direction of increasing activity (Mandal et al. 2017). The observed swirling patterns are similar to structures observed in active turbulence exhibited by a fluid of active rods (Wensink et al. 2012; Giomi 2015), and it is possible that the dynamical heterogeneity exhibited by the active glass is a remnant signature of the turbulent fluid.

More recently, an interesting emerging direction of investigation in active glassy matter has

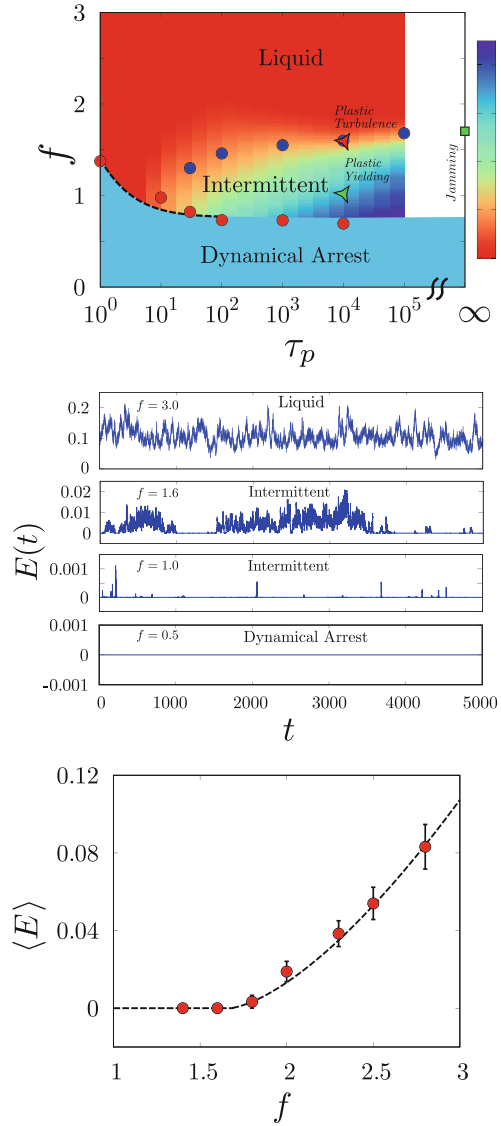


Dense Active Matter, Fig. 2 Active vs passive supercooled liquid (Adapted from Ref. Mandal et al. 2017). (left) Streamlines of displacement field computed over the relaxation timescale τ_α with the underlying colormap reflecting the corresponding values of the spatially varying vorticity. (right) Map showing the magnitude of

displacement during the same time window, with blue particles being the fastest and black particles being the slowest. The top panel corresponds to the active system displaying large-scale vortical structures and extensive spatial heterogeneity, in contrast to the passive system shown in the bottom panel

been the so-called extreme limit wherein the magnitude of the propulsion force f is higher than that of interparticle or thermal forces and the direction of the propulsion force persists over times τ_p longer than characteristic relaxation times of the system in the absence of activity. This aspect has been numerically explored (Mandal et al. 2020) using a two-dimensional athermal assembly of soft-interacting active Brownian particles, each of mass m and driven by a stochastic self-propulsion force $\mathbf{f} = f\mathbf{n}$ whose direction $\mathbf{n}$ undergoes rotational diffusion. Extreme activity is attained when (a) the magnitude of the active force is larger than both thermal forces and the typical force exerted on a particle by the other particles, and (b) the persistence time τ_p is larger than the characteristic relaxation time of the system in the absence of activity. In the athermal limit, condition (b) above is replaced by $Pe \gg 1$ where Pe is an active Péclet number defined as $Pe \equiv f\tau_p/(\gamma\sigma)$ (γ is a friction coefficient and σ is the particle size).

For small values of τ_p , as was discussed earlier, the system transforms from a fluid at high f to a glassy state at low f . The phase boundary is well described by an active generalization of RFOT theory (see section “Theoretical Studies”). This is illustrated in the phase diagram shown in the left panel of Fig. 3. For intermediate values of the persistence time $\tau_p \gtrsim 10^3$, the variation of the time series of the system’s kinetic energy with changing active force marks the evolution of the system through different dynamical regimes; see the middle panel of Fig. 3. At large forcing, it shows random fluctuations. However, as the forcing is decreased, the time series starts becoming intermittent, with periods of bursts followed by quiescence. The gap between these periods of bursts increases with decreasing forcing, and eventually the system gets dynamically arrested as f is decreased even further. The single particle dynamics become more heterogeneous as the phase boundary is crossed (Mandal et al. 2020). Deep inside the intermittent phase, the spikes in the time series of the kinetic energy correspond to the occurrence of local plastic events resulting from the local shear induced via the internal stirring at the scale of the active particles (Mandal et al. 2020).



Dense Active Matter, Fig. 3 Extreme active matter (Adapted from Ref. Mandal et al. 2020). (top) Phase diagram showing different dynamical regimes in the persistence time τ_p vs active forcing f plane. (middle) Time series of kinetic energy, $E(t)$, showing increasing intermittency with decreasing f , for $\tau_p = 10^4$. (bottom) In the limit of infinite persistence time, variation of the mean kinetic energy, $\langle E \rangle$, with forcing f . The system transits to a jammed state as f is decreased below $f^*(\infty) = 1.6$, with $\langle E \rangle \sim |f - f^*(\infty)|^{3/2}$ near $f = f^*(\infty)$

An interesting limit is the case of infinite persistent time of the active particles, that is, where the direction of the active force on each particle does not change with time. In this limit, above a

threshold forcing, $f^*(\infty)$, the system of particles behaves like a fluid, and below this threshold, it reaches an arrested state, consistent with similar observations in the vicinity of the jamming transition for soft harmonic disks (Liao and Xu 2018). On the approach to this arrested state, corresponding to the formation of a force-balanced configuration (Mandal et al. 2020), the kinetic energy vanishes as $\sim |f - f^*(\infty)|^{3/2}$; see the right panel of Fig. 3. A similar yielding transition was also observed (Morse et al. 2020) for the case of athermal quasi-static persistent random displacement, whereby a link to the response under macroscopic shear has also been outlined.

Further studies have tried to explore the aging dynamics in the presence of activity (Janssen et al. 2017), and different aging behavior has been observed for small and large persistence times (Mandal and Sollich 2020), with the former more similar to aging observed during thermal quenches and the latter exhibiting a two-step process with active athermal aging at short times and activity-driven aging at late times.

Theoretical Studies

Most theoretical studies of dense active matter are based on modifications of theoretical descriptions of passive glass-forming liquids (Berthier and Biroli 2011; Lubchenko and Wolynes 2007) to include the effects of activity. The nonequilibrium nature of active systems is not explicitly taken into account in these descriptions. The simplest among these is the “effective temperature” description (Fily et al. 2014) in which the effects of active forces are represented in terms of an “active temperature” that adds to the bath temperature. The active force $\mathbf{f}_i$ in Eq.(1) differs from the thermal noise $\mathbf{y}_i$ in that it has a nonzero correlation time τ_p . If τ_p is small compared to the characteristic time-scales of the system, then the active force can be treated (Mandal et al. 2016) as additional thermal noise corresponding to an active temperature T_a that is proportional to $f^2\tau_p$. The behavior of the active system at temperature T is then assumed to be the same as that of the corresponding passive system at effective temperature $T_{eff} = T + T_a$.

A similar expression for the effective temperature may be obtained from an exact analytic treatment (Mandal et al. 2016; Szamel 2014) of the overdamped dynamics of a particle in a harmonic potential in the presence of an active force with correlation time τ_p . This simple description provides a qualitative understanding of several simulation results (Mandal et al. 2016) obtained for relatively small values of f and τ_p . The line drawn through the data points for the transition temperature in the middle panel of Fig. 1 was obtained from this description.

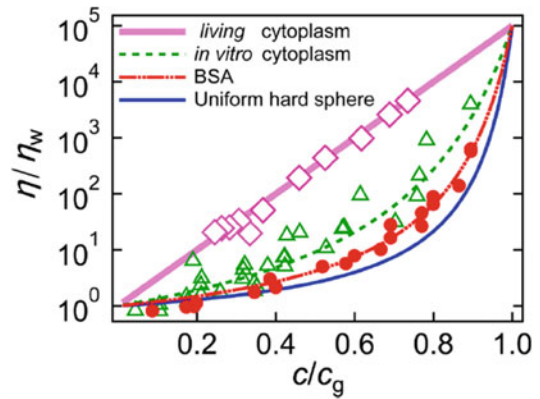
A more detailed description of the dynamics of dense active systems involves an extension (Nandi et al. 2018) of the Random First Order Transition (RFOT) theory (Berthier and Biroli 2011; Lubchenko and Wolynes 2007) of passive glassy dynamics. In the RFOT theory, the structural relaxation time is predicted to diverge at a putative thermodynamic glass transition temperature T_K (also known as the Kauzmann temperature) at which the configurational entropy density s_c associated with the multiplicity of local minima of the potential energy of the system goes to zero. Strictly speaking, s_c is not a well-defined quantity for active systems because they are not in equilibrium. Nevertheless, using a physically reasonable definition of s_c and a mean-field treatment in which the many-particle dynamics is approximated by that of an active particle in a harmonic cage potential produced by its neighbors, an expression for s_c for an active system, characterized by the activity parameters f and τ_p , can be obtained. The dependence of the relaxation time on the activity parameters f and τ_p , obtained by using the expression for s_c in the passive RFOT relation between s_c and the relaxation time, was found to provide a good description of the results of several simulations. The dashed line separating liquid and dynamically arrested phases in the phase diagram shown in the left panel of Fig. 3 was obtained from this theory. The active RFOT theory also resolved apparently contradictory results for the effects of activity on the fragility obtained from different simulations. However, substantial deviations of the predicted results from those obtained from simulations were found for relatively large values of f and τ_p . A recent modification (Mandal et al. 2021) of the active

RFOT theory to include nonperturbative effects arising from a large f has reduced this discrepancy between analytic and simulation results.

Mode coupling theories (Das 2004) of the dynamics of passive glass-forming liquids have also been extended to include the effects of activity (Szamel et al. 2015; Szamel 2016; Nandi and Gov 2017; Liluashvili et al. 2017; Szamel 2019). These theories start from the microscopic equations of motion or the equations of fluctuating hydrodynamics and make certain uncontrolled approximations to obtain analytic results for various time-dependent correlation functions. For passive glass-forming liquids, mode coupling theories provide an accurate description of the dynamics in the weakly super-cooled regime but fail to describe the behavior at lower temperatures. Several studies have used this formalism to look into the effects of activity on the dynamics. The predictions of these studies on the dependence of the dynamics on the activity parameters seem to depend on the nature of the approximations made in deriving the results, the details of the self-propagation mechanism, and the presence or absence of thermal noise. More work is needed to sort out these issues.

Comparison with Experiments

The simple model systems considered in theoretical studies do not provide a realistic description of biological active matter studied in experiments. Nevertheless, some of the results obtained from analytic and numerical studies of these simple models are found to be qualitatively similar to those of experiments on biological systems. For example, the dependence of the fragility parameter on the strength f of the active force found in simulations (Mandal et al. 2016) (see the bottom panel of Fig. 1) and the active RFOT theory (Nandi et al. 2018) is quite similar to that observed in experiments on *in vitro* and living cytoplasm (Nishizawa et al. 2017) – in both cases, the fragility decreases as the activity is increased (see Fig. 4). It has been shown in Ref. (Henkes et al. 2020) that several features of experimentally observed displacement and velocity correlations in epithelial cell



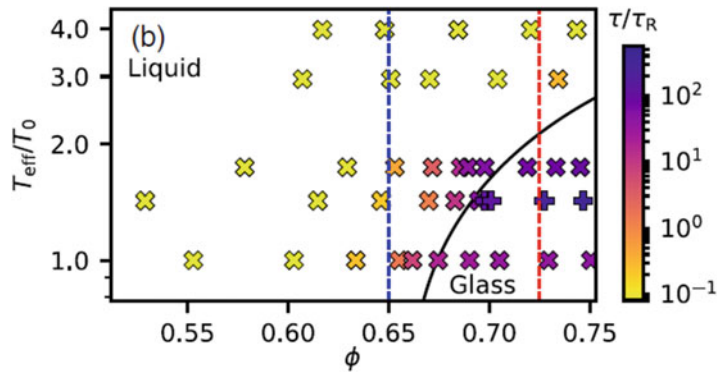
Dense Active Matter, Fig. 4 Viscosity (scaled by the viscosity of water) as a function of scaled concentration for BSA – a globular protein – (red circles and the dash-dot-dot curve), for cell extracts from *E. coli* (green triangles and the dotted curve), and for cytoplasm in a living cell (pink diamonds and the solid line). Higher curvature of the plot indicates larger fragility (from Ref. Nishizawa et al. 2017). The dependence of the fragility on activity is similar to that shown in the bottom panel of Fig. 1

monolayers can be reproduced in theoretical and numerical studies of simple models. Another example is the observation (Park et al. 2015) of a jamming transition in confluent monolayers of human bronchial epithelial cells at a value of a geometrical parameter associated with cell shapes that is close to the value at which a similar transition occurs in simulations (Bi et al. 2015) of the vertex model mentioned above.

There is a closer connection between theoretical models and experimentally studied systems of synthetic active matter. As shown in Fig. 5, the phase diagram obtained in an experimental study of a system of Janus colloids (Klongvessa et al. 2019a) for which the packing fraction is the control parameter is qualitatively similar to that found in simulations (Mandal et al. 2016) of a model of thermally driven active particles (see the middle panel of Fig. 1). In both cases, the activity is found to promote fluidization in a similar way.

Conclusion and Future Directions

This short review attempts to provide a summary of the current state of affairs in the developing field of dense active matter. The primary interest in studies



Dense Active Matter, Fig. 5 Phase diagram of a two-dimensional system of Janus colloids in the activity (T_{eff}/T_0) vs. packing fraction (ϕ) plane (from Ref. Klongvessa et al. 2019a). The colorbar indicates the value of the relaxation time. Increasing the packing

fraction in this system is similar to decreasing the temperature in a thermally driven system. This phase diagram is similar to that in the middle panel of Fig. 1 – activity promotes fluidization in both cases

of dense active matter derives from the biological importance of understanding the behavior of two- and three-dimensional collections of cells. As discussed above, analytic and computational studies of simple models of active matter are beginning to make contact with experiments on cell assemblies. However, there is a need for incorporating biologically important features in these models. Experiments on synthetic active systems that are closer to the theoretical models are also being performed. More effort in this direction would make it easier to connect theoretical predictions with experimental results. On the theoretical side, the behavior of dense active matter with relatively small values of f and τ_p is fairly well-understood. However, there is little theoretical understanding of several interesting features observed in simulations (Mandal et al. 2020) of extreme active matter with large f and/or τ_p . More theoretical work and experiments on extreme active matter would be most welcome.

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Ultracold Atomic Gases: Novel States of Matter

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Article Outline

Glossary

Definition of the Subject

Introduction

One-Dimensional Lattices

Phase-Locking Transition of Coupled Low-Dimensional Superfluids

Bose-Fermi Mixtures in Two-Dimensional Optical Lattices

Conclusions

Bibliography

Glossary

Bose-Einstein condensation (BEC) Low-temperature phase of systems of identical bosons, characterized by superfluidity.

Boson Particles with integer spin $S = 0, 1, 2, \dots$. Mediators of interactions, such as photons and gluons, are bosons. Objects made of an even number of fermions are bosons: positronium (electron + positron), meson (two quarks), ⁸⁷Rb (37 protons, 48 neutrons, and 37 electrons), and ⁷Li (3 protons, 4 neutrons, 3 electrons).

Cooper pairs At low temperatures and for attractive interactions, fermions form a superconducting state, in which fermions form pairs which condense.

Evaporative cooling To slow the atoms down further, to the μK regime, one applies radio frequency radiation that flips the internal state to a

high-field seeking, i.e., non-trapped, state in such a way that only atoms of high kinetic energy can escape. Due to thermalization, this leads to cooling of the remaining atomic ensemble.

Fermi surface Since fermions obey Pauli's exclusion principle, the ground state of N noninteracting fermions in d -dimensions is the state with the N lowest energy states occupied. In momentum space the last occupied state and the first unoccupied state define a surface of dimensions $d - 1$, called the Fermi surface.

Fermion Particles with half-odd integer spin $S = 1/2, 3/2, 5/2, \dots$. Examples include elementary particles such as electrons and quarks. Objects made of an odd number of fermions are also fermionic, such as protons, ⁴⁰K (19 protons, 21 neutrons, and 19 electrons), and ⁶Li (3 protons, 3 neutrons, and 3 electrons).

Laser cooling In a typical experimental setup, the atoms are cooled to the regime of $10^2 \mu\text{K}$, by using pairs of counterpropagating laser beams that are slightly red-detuned below an atomic transition. Due to the Doppler effect, the atoms can only absorb a photon if they travel toward the beam with a high velocity. From that process the atoms experience a recoil, which slows them down.

Magnetic trap The atoms are trapped by applying a spatially inhomogeneous magnetic field. This field leads to an energy shift due to the Zeeman effect, which the atoms experience as an external potential, for large energy splittings of the magnetic levels. Different geometric designs are in use, such as the TOP trap or the Ioffe-Pritchard trap.

Nesting Fermi surface with portions that are parallel. The vector that connects different parallel portions is called the nesting vector $\vec{Q}$.

Optical lattice Counterpropagating laser beams create a standing wave field, which the atoms experience as a periodic potential, due to the ac Stark shift. If the temperature and all energy scales are small compared to the energy splitting due the spatial confinement in each well,

this system is well approximated by a Hubbard model, i.e., by taking into account nearest-neighbor hopping and on-site interaction.

Definition of the Subject

The work presented in this entry belongs to the recently emerging interface of atomic physics and condensed matter theory. One of the crucial connections between these fields is the fact that ultracold atom ensembles in optical lattices, i.e., periodic potentials provided by standing waves of laser light, are well described by Hubbard models, the quintessential model of many-body theory. Therefore, these experiments allow for the study of many-body effects in a well-defined and tunable environment.

The subject of this entry is the study of quantum phases of ultracold atoms in optical lattices. The objective is to propose experimental configurations, such as what lattice geometry or which types of atoms to use, for which unusual many-body effects can be found. Besides the applicability to ultracold atom systems and given the generic nature of the underlying models, the resulting phases are also of interest in solid-state systems.

Using techniques such as a numerical implementation of functional renormalization group equations and Luttinger liquid theory, we find the phase diagrams of various low-dimensional systems of different geometry and discuss how the various phases could be detected.

Introduction

The technology of cooling and trapping atomic ensembles has been one of the most important developments in physics over the last decades. It has been a critical ingredient in creating Bose-Einstein condensates (Anderson et al. 1995; Davis et al. 1995), improving atomic clocks (Phillips et al. 1996), and studying atomic properties (Jones et al. 1996; Lett et al. 1995). A new direction in this development was the realization of the Mott insulator transition (Greiner et al. 2002) with ultracold atoms, which demonstrated that these systems can be used to create various types

of quantum phases in a tunable and well-defined environment. The subsequent progress that has been made in controlling and manipulating ensembles of ultracold atoms (Köhl et al. 2005; Mandel et al. 2003a, b; Stöferle et al. 2004) was followed by a number of experiments to create and study more and more sophisticated many-body effects, such as fermionic superfluids (Greiner et al. 2003; Jochim et al. 2003; Zwierlein et al. 2003), one-dimensional strongly correlated Fermi and Bose systems (Kinoshita et al. 2004; Moritz et al. 2005; Paredes et al. 2004), or noise correlations in interacting atomic systems (Altman et al. 2004; Fölling et al. 2005; Greiner et al. 2005; Mathey et al. 2008a). These developments established the notion of “engineering” many-body states in a tunable environment, i.e., manipulating ensembles of ultracold atoms in optical lattices.

This entry further explores this development. The first step of creating novel states of matter is to determine the phase diagram of the system under consideration. For this purpose we use Luttinger liquid theory for studying one-dimensional quantum systems and two-dimensional thermal systems and functional renormalization group equations to study two-dimensional quantum systems, which are both sophisticated methods that generate a lot of insight into the physics of these systems.

This entry contains three main sections, which can be read independently of each other, organized as follows: In section “[One-Dimensional Lattices](#),” we first study the phase diagram of an incommensurate Bose-Fermi mixture in one dimension, which can be understood as a Luttinger liquid of polarons (see Mathey et al. 2004; Mathey and Wang 2007). We then broaden the scope of this study to include the effects of commensurate densities (see Mathey 2007). In section “[Phase-Locking Transition of Coupled Low-Dimensional Superfluids](#),” we study the phases of two coupled two-dimensional superfluids, and we propose how the phase-locking transition of such systems can be used to realize the Kibble-Zurek mechanism, i.e., to create topological defects by ramping across a phase transition (see Mathey et al. 2008b). In section “[Bose-Fermi Mixtures in Two-Dimensional Optical Lattices](#),” we use a numerical implementation of functional renormalization group equations to

study the phase diagrams of Bose-Fermi mixtures in optical lattices in two dimensions. For both, a square and a triangular lattice, we find a rich structure of competing phases (see Klironomos and Tsai 2007; Mathey et al. 2006, 2007).

One-Dimensional Lattices

The theory of one-dimensional many-body systems has been a highly active and fascinating field of physics for many decades, the centerpiece of which is the notion of the Luttinger liquid (Giamarchi 2004; Gogolin et al. 1998; Solyom 1979). In this section, we propose several systems that display various features of Luttinger liquids, such as quasi-long-range order, competing orders, and Kosterlitz-Thouless transitions due to commensurate densities, as will be explained.

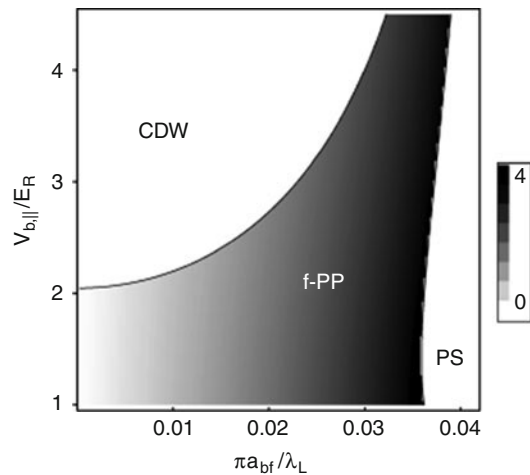
Recent advances in controlling ultracold atoms lead to the realization of truly one-dimensional systems and the study of many-body effects therein. Important benchmarks, such as the Tonks-Girardeau gas (Kinoshita et al. 2004; Paredes et al. 2004) and the Mott transition in one dimension (Stöferle et al. 2004), have been achieved by trapping bosonic atoms in tight tubes formed by an optical lattice potential. Novel transport properties of one-dimensional lattice bosons have been studied using these techniques (Fertig et al. 2004). More recently, a strongly interacting one-dimensional Fermi gas was realized using similar trapping methods (Moritz et al. 2005). Interactions between the fermion atoms were controlled by tuning a Feshbach resonance in these experiments. On the theory side, numerous proposals were given for realizing a variety of different phases in ultracold Fermi systems (Cazalilla et al. 2005; Fuchs et al. 2004; Recati et al. 2003), Bose-Fermi mixtures (Cazalilla and Ho 2003; Mathey et al. 2004; Mathey and Wang 2007; Sengupta and Pryadko 2005), and Bose-Bose mixtures (Isacsson and Girvin 2005; Isacsson et al. 2005).

In the first part of this section, we describe the phase diagram of an incommensurate Bose-Fermi mixture; in the second part we consider the effect of commensurate fillings.

Luttinger Liquid of Polarons in One-Dimensional Bose-Fermi Mixtures

In this section we investigate one-dimensional (1D) Bose-Fermi mixtures (BFM) using bosonization (Cazalilla 2004; Haldane 1981). The resulting quantum phases can be understood by introducing polarons, i.e., atoms of one species surrounded by screening clouds of the other species. In our analysis the polarons emerge as the most well-defined quasi-particles in the interacting system, while quantum phases of the system arise from a competition of various ordering instabilities of such polarons. The phase diagrams we obtain show a remarkable similarity to the Luttinger liquid phase diagrams of 1D interacting electron systems (Solyom 1979; Voit 1995), suggesting that 1D BFM may be understood as Luttinger liquids of polarons.

To illustrate the results of this section, we show a typical phase diagram for a BFM in an optical lattice in Fig. 1, as a function of experimentally controlled parameters. We consider two types of atoms, one fermionic and one bosonic, moving in a lattice potential with the amplitude $V_{b,\parallel}$ (see

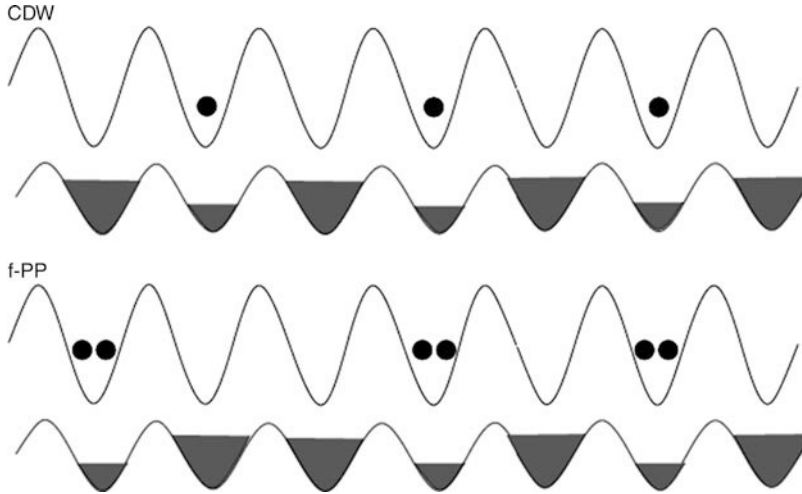


Ultracold Atomic Gases: Novel States of Matter, Fig. 1 Phase diagram for a mixture of bosonic and spinless fermionic atoms in a 1D optical lattice. *Shading* in the f-PP phase describes the strength of the bosonic screening cloud (2λ , see Eq. 4) around a pair of fermions. λ_L and E_R are, respectively, the lattice period and recoil energy. Other parameters used for this figure are (see text for notations, Mathey and Wang (2007) for details) as follows: $v_b = 4$, $v_f = 0.5$, $V_{b,\perp} = V_{f,\perp} = 20E_R$, $V_{f,\parallel} = 2E_R$, and boson-boson scattering length $a_{bb} = 0.01\lambda_L$.

Mathey and Wang 2007), and interacting via a short-ranged interaction characterized by the scattering length a_{bf} between bosons and fermions. We use these parameters, the scattering length a_{bf} and the strength of the longitudinal optical lattice for bosonic atoms ($V_{b,\parallel}$) as tuning parameters in Fig. 1. (In this paper, we use $V_{f/b,\parallel(\perp)}$ to denote the optical lattice potential experienced by fermionic/bosonic atoms in the longitudinal (perpendicular) directions. Independent tuning of the optical lattices for two species of atoms can be achieved even with a single pair of lasers by controlling the laser detuning and intensity separately.) For relatively weak interactions and slow bosons (i.e., large $V_{b,\parallel}$), the system is in the charge-density-wave (CDW) phase, in which the densities of fermions and bosons have a periodic modulation. (We note that in a homogeneous 1D system, only quasi-long-range order for CDW phase is possible. However, the inhomogeneous trap boundary in a realistic experiment can pin the CDW phase to generate a true density modulation.) For very strong interactions the system is unstable to phase separation (PS) (Albus et al. 2003; Bijlsma et al. 2000; Cazalilla and Ho 2003). The two regimes are separated by a p -wave pairing phase of fermionic

polarons (f -PP). Our analysis is carried out for the most promising system of atoms in an optical lattice. However, qualitative results should also apply to atoms in a tight 1D cigar-shaped magnetic trap (Görlitz et al. 2001). A sketch of the two phases is shown in Fig. 2.

The essence of the bosonization procedure is to diagonalize the effective low-energy Hamiltonian, which allows for the exact calculation of all relevant correlation functions. The phase diagrams are determined by finding the order parameter which has the most divergent susceptibility (Solyom 1979; Voit 1995). Bosonization approach has been applied to BFM in Cazalilla and Ho (2003). However, that work did not consider the formation of polarons and, as a result, did not describe most of the quantum phases discussed here. The present system also has a close analogy to 1D electron-phonon systems discussed previously (see, e.g., Voit and Schulz 1987). A qualitative difference of the electron-phonon system is that the sound velocity is usually much smaller than the Fermi velocity, whereas for a BFM the velocity of the phonon modes (of the bosonic condensate) can be larger than the Fermi velocity. We also note that the 1D



Ultracold Atomic Gases: Novel States of Matter, Fig. 2 Illustration of the two phases that occur in a BFM with spinless fermions, CDW, and f -PP. In the CDW phase the system develops a $2k_F$ density modulation in both the fermionic and the bosonic liquids. In the f -PP phase, the

fermions form polarons, indicated by the reduced bosonic density in their vicinity, that is, their polarization cloud. This polarization leads to an effective attractive interaction, which causes these fermionic polarons to pair up and form a superfluid state

p -wave superfluid we obtain here may be of relevance to a recent proposal for quantum computation (Kitaev 2000).

We now give an overview over the, somewhat technical, derivation of this phase diagram, before we discuss issues concerning the experimental realization and detection of these phases and conclude. We consider a mixture of spinless fermionic (f) and bosonic (b) atoms. For a sufficiently strong optical potential, the microscopic Hamiltonian is given by a single-band Hubbard model:

$$H = - \sum_{\langle ij \rangle} (t_b b_i^\dagger b_j + t_f f_i^\dagger f_j) - \sum_i (\mu_f n_{f,i} + \mu_b n_{b,i}) + \frac{U_b}{2} \sum_i n_{b,i} (n_{b,i} - 1) + U_{bf} \sum_i n_{b,i} n_{f,i}, \quad (1)$$

where $n_{b/f,i}$ are the boson-fermion density operators with $\mu_{b/f}$ being their chemical potentials. The tunneling amplitudes $t_{b/f}$ and the particle interactions U_b and U_{bf} can be expressed explicitly in terms of the s -wave scattering lengths, the laser beam intensities, and the atomic masses (Jaksch et al. 1998). For simplicity we assume that the filling fraction of fermions $v_f \equiv \langle n_{f,i} \rangle$ is not commensurate with the lattice or with the filling fraction of bosons v_b . Therefore, we can neglect lattice-assisted backward/Umklaapp scattering. The Fermi momentum and velocity are given by $k_f = \pi v_f$ and $v_f = 2t_f \sin(k_f)$, respectively.

In Haldane's bosonization approach (Cazalilla 2004; Haldane 1981), 1D fermion and boson operators can be represented by

$$f(x) = [v_f + \Pi_f]^{1/2} \sum_{m=-\infty}^{\infty} e^{(2m+1)i\Theta_f} e^{i\Phi_f} \quad \text{and} \quad b(x) = [v_b + \Pi_b]^{1/2} \sum_{m=-\infty}^{\infty} e^{2mi\Theta_b} e^{i\Phi_b}, \quad \text{where } x \text{ is a}$$

continuous coordinate that replaces the site index i . The operators $\Pi_{f/b}(x)$ and $\Phi_{f/b}(x)$ are the bosonized density and phase fluctuation operators. The $\Theta_{f/b}(x)$ fields are given by $\Theta_{f/b} \equiv \pi v_{f/b} x + \pi \int^x dy \Pi_{f/b}(y)$. The low-energy effective Hamiltonian thus can be written as

$$H_{\text{eff}} = \sum_{\alpha=b,f} \frac{v_\alpha}{2} \int dx \left[\frac{K_\alpha}{\pi} (\partial_x \Phi_\alpha)^2 + \frac{\pi}{K_\alpha} \Pi_\alpha^2 \right] + U_{bf} \int dx \Pi_b \Pi_f + \frac{2G}{2\pi} \int dx \left[\pi^2 \Pi_f^2 - (\partial_x \Phi_f)^2 \right]. \quad (2)$$

where v_b and K_b are the phonon velocity and Luttinger exponent of the bosons and $K_f = 1$ for noninteracting fermion atoms.

To obtain the last term of H_{eff} , we have integrated out the high-energy ($2k_f$) phonons within the instantaneous approximation (i.e., assuming $v_b \gg v_f$). $G \equiv g_{2kf}^2 / \omega_{2kf}$, where ω_k is the (Bogoliubov) phonon energy dispersion (Tsuchiya and Griffin 2003) and $g_k = U_{bf} \sqrt{v_b \epsilon_{b,k} / 2\pi \omega_k}$ is the fermion-phonon (FP) coupling vertex with $\epsilon_{b,k}$ being the noninteracting boson band energy. In the long wavelength limit, we have a conventional FP coupling $g_k = g|k|^{1/2}$ with $g \equiv U_{bf} \sqrt{K_b} / 2\pi$. The effective Hamiltonian, Eq. 2, is quadratic and can be diagonalized (Engelsberg and Varga 1964). The resulting two eigenmode velocities are given by Cazalilla and Ho (2003)

$$v_{a,A}^2 = \frac{1}{2} (v_b^2 + \tilde{v}_f^2) \pm \frac{1}{2} \sqrt{(v_b^2 + \tilde{v}_f^2) + 16\tilde{g}^2 v_b \tilde{v}_f}, \quad (3)$$

where $\tilde{v}_f \equiv (v_f^2 - 4G^2)^{1/2}$ and $\tilde{g} \equiv g e^\theta$ with $e^\theta = ((v_f - 2G)/(v_f + 2G))^{1/4}$. When the FP coupling g becomes sufficiently strong, the eigenmode velocity v_A becomes imaginary, indicating an instability of the system. This instability corresponds to phase separation (global collapse) for positive (negative) U_{bf} (Cazalilla and Ho 2003).

To understand the nature of the many-body state of BFM outside of the instability region, we analyze the long-distance behavior of the correlation functions. For the bare bosonic and fermionic particles, we find $\langle b(x) b^\dagger(0) \rangle \sim |x|^{-\frac{1}{2}K_b^{-1}}$ and $\langle f(x) f^\dagger(0) \rangle \sim \cos(k_f x) |x|^{-\frac{1}{2}(K_b + K_f^{-1})}$. (Here we defined $K_\beta \equiv e^{2\theta} \tilde{v}_f (\cos^2 \psi / v_A + \sin^2 \psi / v_b)$, $K_\delta \equiv K_b v_b (\sin^2 \psi / v_A + \cos^2 \psi / v_b)$, $K_\gamma^{-1} \equiv e^{-2\theta} / \tilde{v}_f$

($v_A \cos^2 \psi + v_a \sin^2 \psi$) $K_c^{-1} \equiv K_b^{-1}/v_b(v_A \sin^2 \psi + v_a \sin^2 \psi)$, $K_{\beta\delta} = e^\theta \sqrt{K_b \tilde{v}_f v_b} \sin(2\psi)/2(1/v_a - 1/v_A)$, and $K_{\gamma\epsilon}^{-1} = e^{-\theta} / \sqrt{K_b \tilde{v}_f v_b} \sin(2\psi)/2(v_a - v_A)$. ψ is given by $\tan 2\psi = 4\tilde{g}(v_b \tilde{v}_f)^{1/2}/(v_b^2 - \tilde{v}_f^2)$. These expressions are obtained from diagonalizing H_{eff} . For details see Mathey and Wang (2007). To describe particles dressed by the other species, we introduce the composite operators

$$\tilde{f}(x) \equiv e^{-i\lambda\Phi_b(x)} f(x), \quad \tilde{b}(x) \equiv e^{-i\eta\Phi_f(x)} b(x), \quad (4)$$

with λ and η being some real numbers. The correlation functions of these operators are given by $\langle \tilde{f}(x) \tilde{f}^\dagger(0) \rangle \sim \cos(k_f x) |x|^{-\frac{1}{2}(K_\beta + \lambda^2 K_c^{-1} + K_\gamma^{-1} - 2\lambda K_{\gamma\epsilon}^{-1})}$ and $\langle \tilde{b}(x) \tilde{b}^\dagger(0) \rangle \sim |x|^{-\frac{1}{2}(K_c^{-1} + \eta^2 K_\gamma^{-1} - 2\eta K_{\gamma\epsilon}^{-1})}$ (Here we defined $K_\beta \equiv e^{2\theta} \tilde{v}_f (\cos^2 \psi / v_A + \sin^2 \psi / v_a)$, $K_\delta \equiv K_b v_b (\sin^2 \psi / v_A + \cos^2 \psi / v_a)$, $K_\gamma^{-1} \equiv e^{-2\theta} / \tilde{v}_f (v_A \cos^2 \psi + v_a \sin^2 \psi)$, $K_c^{-1} \equiv K_b^{-1} / v_b (v_A \sin^2 \psi + v_a \sin^2 \psi)$, $K_{\beta\delta} = e^\theta \sqrt{K_b \tilde{v}_f v_b} \sin(2\psi)/2(1/v_a - 1/v_A)$, and $K_{\gamma\epsilon}^{-1} = e^{-\theta} / \sqrt{K_b \tilde{v}_f v_b} \sin(2\psi)/2(v_a - v_A)$. ψ is given by $\tan 2\psi = 4\tilde{g}(v_b \tilde{v}_f)^{1/2}/(v_b^2 - \tilde{v}_f^2)$. These expressions are obtained from diagonalizing H_{eff} . For details see Mathey and Wang (2007).) We observe that the exponents of the correlation functions are maximized for $\lambda_c = K_\epsilon/K_{\gamma\epsilon}$ and $\eta_c = K_\gamma/K_{\gamma\epsilon}$. From now on we will use Eq. 4 with λ_c and η_c to construct polaronic particles. In the limit of weak interactions, we have $\lambda_c \rightarrow U_{bf}/U_b$ and $\eta_c \rightarrow 2U_{bf}/\pi v_b$. This result can be understood by a simple density counting argument that a fermionic polaron (f -polaron) locally suppresses (enhances) a bosonic cloud by λ_c particles, whereas a bosonic polaron (b -polaron) depletes (enhances) the fermionic system by η_c atoms for positive (negative) g .

The polaronic operators defined in Eq. 4 can also be introduced via the canonical polaron transformation (CPT), which is often used in polaron theory (Alexandrov and Mott 1995; Mahan 1990). The CPT

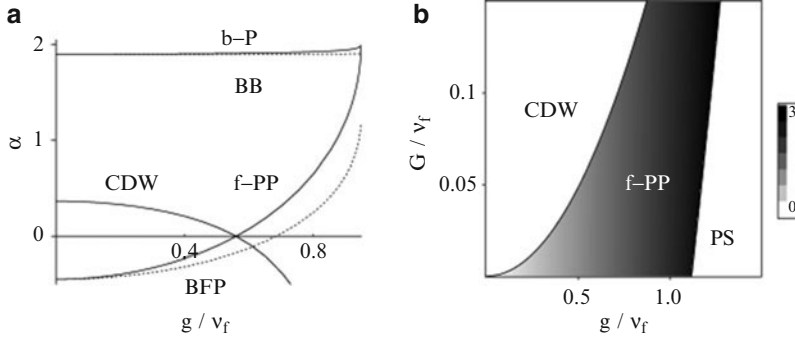
$$-i\lambda \sum_{k \neq 0} (F_k \beta_k \rho_k^\dagger + \text{h.c.})$$

operator is given by $U = e^{\quad}$, where β_k is the phonon annihilation operator, ρ_k is the fermion density operator, F_k is some function of wavevector k , and λ specifies the strength of the phonon dressing. When applied to a fermion

operator, the CPT transforms it to a polaron operator, $U^{-1}f(x)U = f(x) \exp \left[-i\lambda \sum_{k \neq 0} (F_k \beta_k e^{-ik \cdot x} + \text{h.c.}) \right]$

(Alexandrov and Mott 1995; Mahan 1990), which is the same as Eq. 4, provided that one takes $F_k = \sqrt{2\pi/(K_b |k| L)} \text{sgn}(k)$. (Note that in 1D fermionic systems, density operators correspond to Luttinger bosons.) We note, however, unlike in ordinary polaron theory, where further approximations after the CPT have to be made (Alexandrov and Mott 1995; Mahan 1990), in the 1D BFM system we consider here, the full low energy quantum fluctuations have been included via bosonization method and exact diagonalization of the resulting Hamiltonian Eq. 2. This allows for an essentially exact determination of the polarization parameter λ .

Now we study the many-body ground state phase diagram of a 1D BFM, which is characterized by specifying the order parameters that have the slowest long-distance decay of the correlation functions (Solyom 1979; Voit 1995). Two types of ordering were found to occur: $2k_f$ ordering due to a Peierls-type instability and f -polaron pairing due to their effective attractive interactions induced by the screening clouds; see Fig. 2. For the $2k_f$ CDW order parameter, $O_{\text{CDW}} = f_L^\dagger f_R$, we find $\alpha_{\text{CDW}} = 2 - 2K_\beta$, and for the f -polaron pairing field, $O_{f\text{-PP}} = \tilde{f}_L \tilde{f}_R$, we obtain $\alpha_{f\text{-PP}} = 2 - 2[\lambda_c^2 K_c^{-1} + K_\gamma^{-1} - 2\lambda_c K_{\gamma\epsilon}^{-1}]$. We did not include polaron dressing in O_{CDW} , since this operator has no net fermionic charge and the exponent of O_{CDW} does not change if we replace f by $\tilde{f}$. Scaling exponents shown in Fig. 3a demonstrate that divergencies of the CDW and f -PP susceptibilities (corresponding to positive α) are mutually exclusive and cover the entire phase diagram outside the PS regime. In the same figure, we also show the scaling exponents calculated for bare fermion pairing ($O_{\text{BFP}} = f_L^\dagger f_R$), bare boson condensate ($O_{\text{BB}} = b$), and b -polaron condensate ($O_{b\text{-P}} = \tilde{b}$). It is easy to see that the polaronic order parameters always have larger exponents than their counterparts constructed with bare atoms, showing the stability of polaronic quasi-particle in a 1D BFM system. Moreover, the necessity to consider f -polaron pairing instead of bare fermion pairing is further



Ultracold Atomic Gases: Novel States of Matter, Fig. 3 Ground state of a BFM with spinless fermions. (a) Scaling exponents of different order parameters (see the text). Parameters are chosen to be $v_b/v_f = 3$, $K_b = 5$, and

$G/v_f = 0.1$. (b) Global phase diagram for $v_b/v_f = 5$ and $K_b = 10$. Shading density indicates the strength of the screening clouds of a polaron pair, $2\lambda_c$

supported by considering the stability of superfluidity: We introduce a single weak impurity potential in the 1D BFM and determine its relevance by a renormalization group (RG) calculation (Kane and Fisher 1992). We find that the impurity potential is relevant within the CDW phase and irrelevant outside of it. This indicates that there should be a superfluid phase outside of the insulating CDW phase, which supports the existence of f -polaron pairing instead of bare fermion pairing according to Fig. 3a.

In Fig. 3b we show a global phase diagram of a BFM considering the FP coupling (g) and effective fermion-fermion interaction (G) as independent variables. One can see that the polaronic effects and the associated pairing phase are important when FP coupling (g) is large, while the CDW phase dominates when the effective fermion interaction (G) is increased. This phase diagram is very similar to what one finds for spinless electrons in Luttinger liquid theory (Solyom 1979; Voit 1995), where CDW and pairing phase compete with each other in the whole phase diagram. Therefore, one can introduce a Luttinger liquid of polarons to describe BFM in 1D systems. The phase diagram in terms of experimentally controlled parameters was shown in Fig. 1. When considering finite temperature effects in a realistic experiment, we note that the correlation function is cut off by thermal correlation lengths, which are approximately given by $\xi \sim v_f/k_B T$. Therefore, the zero

temperature ground states should appear when $\xi > L$ with L being the system size. This corresponds to a temperature regime of 1 % of the Fermi temperature for systems of approximately 100 sites in the longitudinal direction.

Several approaches can be used to detect the quantum phases discussed above. First, in the CDW phase the fermion density modulation will induce a $2k_f$ density wave in the boson field in addition to the zero momentum condensation so that the CDW phase can be observed as interference peaks at momentum $k = 2k_f$ in a standard time-of-flight (TOF) measurement for bosons. (We note that in a homogeneous 1D system only quasi-long-range order for CDW phase is possible. However, the inhomogeneous trap boundary in a realistic experiment can pin the CDW phase to generate a true density modulation.) Secondly, the polaron pairing phase can be observed by measuring the noise correlation of fermions in a TOF experiment as proposed in Altman et al. (2004). Thirdly, a laser stirring experiment (Onofrio et al. 1999; Raman et al. 1999) can be used to probe the phase transition between the insulating (pinned by trap potential) CDW and the superfluid f -PP phase: One can use a laser beam focused at the center of the cloud and stir such local potential to measure the response of the BFM. If the system is in the pairing phase, the laser beam can be moved through the system without dissipation if only its velocity is slower than some critical value

(Onofrio et al. 1999; Raman et al. 1999). At the f -PP/CDW phase boundary, this critical velocity goes to zero, reflecting a transition to the insulating (CDW) state. This scenario follows from the above described RG analysis of a single impurity potential (Kane and Fisher 1992). Finally, a way to probe the PS boundary could be to measure the dipolar collective oscillations of the system, generated by a sudden displacement of the harmonic trap potential with respect to the lattice potential (Gensemer and Jin 2001; Maddaloni et al. 2000; Vichi et al. 1999). When the system is near the PS boundary, fermion-boson interaction will strongly reduce the frequency of the dipolar mode.

In summary, we used bosonization to investigate the quantum phases of 1D mixtures of bosonic and fermionic atoms involving spinless fermions. The phase diagram that we found can be understood in terms of a Luttinger liquid of polarons. We also described several experimental techniques for probing these quantum phases.

Commensurate Mixtures of Ultracold Atoms in One Dimension

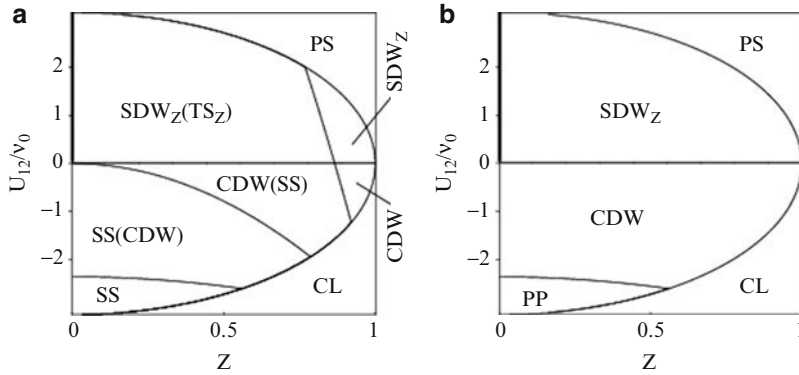
In this section we explore the behavior of ultracold atomic mixtures, confined to one-dimensional (1D) motion in an optical lattice, that exhibit different types of commensurability, by which we mean that the atomic densities and/or the inverse lattice spacing has an integer ratio. Commensurable fillings arise naturally in many ultracold atom systems, because the external trap potential approximately corresponds to a sweep of the chemical potential through the phase diagram and therefore passes through points of commensurability. At these points the system can develop an energy gap, which fixes the density commensurability over a spatially extended volume. This was demonstrated in the celebrated Mott insulator experiment by Greiner et al. (2002), where Mott phases with integer filling occurred in shell-shaped regions in the atom trap. These gaped phases gave rise to the well-known signature in the time-of-flight images and triggered the endeavor of “engineering” many-body states in optical lattices. (Due to the confining trap, the transition is, while visible, “blurred” into a gradual crossover, due to finite size effects and, more

importantly, due to the coexistence of several phases in the trap. This can also be expected for the phase transitions predicted in this entry.) Further examples include the recently created density-imbalanced fermion mixtures (Partridge et al. 2005; Zwierlein et al. 2005) in which the development of a balanced, i.e., commensurate, mixture at the center of the trap is observed.

In 1D, this phenomenon is of particular importance, because it is the only effect that can lead to the opening of a gap, for a system with short-range interactions. In contrast to higher-dimensional systems, where, for instance, pairing can lead to a state with an energy gap, in 1D only discrete symmetries can be broken, due to the importance of fluctuations. Orders that correspond to a continuous symmetry can, at most, develop quasi-long-range order (QLRO), which refers to a state in which an order parameter $O(x)$ has a correlation function with algebraic scaling, $\langle O(x)O(0) \rangle \sim |x|^{-(2-\alpha)}$, with a positive scaling exponent α .

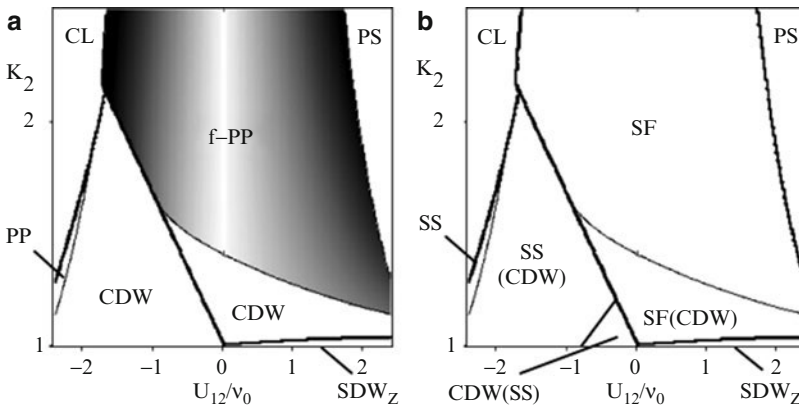
Due to its importance in solid-state physics, the most thoroughly studied commensurate 1D system is the SU(2) symmetric system of spin-1/2 fermions. This system develops a spin gap for attractive interaction and remains gapless for repulsive interaction, as can be seen from a second-order RG calculation. However, the assumed symmetry between the two internal spin states, which is natural in solid-state systems, does not generically occur in Fermi-Fermi mixtures (FFMs) of ultracold atoms, where the “spin” states are in fact different hyperfine states of the atoms. An analysis of the generic system is therefore highly called for. Furthermore, we will extend this analysis to both Bose-Fermi (BFMs) and Bose-Bose mixtures (BBMs), as well as to the dual commensurability, in which the charge field, and not the spin field, exhibits commensurate filling, as will be explained below.

The main results of this section are the phase diagrams shown in Figs. 4 and 5. We find that both attractive and repulsive interactions can open an energy gap. For FFMs the entire phase diagram is gaped, except for the repulsive SU(2) symmetric regime (cf. Cazalilla et al. 2005); for BFMs or BBMs the bosonic liquid(s) need (s) to be close to the hardcore limit, otherwise the



Ultracold Atomic Gases: Novel States of Matter, Fig. 4 (a) Phase diagram of a commensurate FFM or a BBM of hardcore bosons (with the replacement $TS_Z \rightarrow SS$), (b) phase diagram of a BFM with hardcore bosons, in terms of the interaction U_{12} and the parameter $z = |v_1 - v_2|/(v_1 + v_2)$. For both attractive and repulsive interactions, a spin gap opens, except for $z = 0$ and positive interaction. In the attractive regime, a FFM or a BBM shows either singlet pairing or CDW order or a coexistence of these phases and a BFM shows either CDW order or polaron

pairing. For repulsive interaction all mixtures show SDW ordering, with FFMs and BBMs showing subdominant triplet or singlet pairing, respectively, for a large range of z . In the gapless regime, a FFM shows degenerate SDW and CDW order, a BFM shows CDW order for the fermions and SF for the bosons, and a BBM shows SF with subdominant CDW, i.e., supersolid behavior. For very large positive values of U_{12} , the system undergoes phase separation (PS); for very large negative values, it collapses (CL)



Ultracold Atomic Gases: Novel States of Matter, Fig. 5 (a) Phase diagram of a BFM; (b) phase diagram of a BBM with the first species being in the hardcore limit, in terms of U_{12} , and the Luttinger parameter of the second species (K_2), at the fixed velocity ratio $|v_1 - v_2|/(v_1 + v_2) = 0.5$. For large repulsive interaction the system undergoes phase separation (PS); for large attractive interaction the

system collapses (CL). In the regime below the *thick line*, the system opens a gap, i.e., if species 2 is close to the hardcore limit. However, for larger values of K_2 , the gapless phase is restored. Close to the transition, the properties of the fermions, respectively, hardcore bosons, are still affected by the RG flow, leading to CDW order for the fermions and to supersolid behavior for the bosons

system remains gapless. Furthermore, we find a rich structure of quasi-phases, including charge and spin density wave order (CDW, SDW), singlet and triplet pairing (SS, TS), polaron pairing (Mathey et al. 2004; Mathey and Wang 2007), and a supersolid phase, which is the first

example of a supersolid phase in 1D. These results are derived within a Luttinger liquid (LL) description, which treats bosonic and fermionic liquids on equal footing.

We will now classify the types of commensurability that can occur in a system with short-

ranged density-density interaction. We consider Haldane's representation (Cazalilla 2004; Haldane 1981) of the densities for the two species:

$$n_{1/2} = [v_{1/2} + \Pi_{1/2}] \sum_m e^{2mi\Theta_{1/2}}. \quad (5)$$

v_1 and v_2 are the densities of the two liquids and $\Pi_{1/2}(x)$ are the low- k parts (i.e., $k \ll 1/v$) of the density fluctuations; the fields $\Theta_{1/2}(x)$ are given by $\Theta_{1/2}(x) = \pi v_{1/2}x + \theta_{1/2}(x)$, with $\theta_{1/2}(x) = \pi \int^x dy \Pi_{1/2}(y)$. These expressions hold for both bosons and fermions. If we use this representation in a density-density interaction term $U_{12} \int dx n_1(x) n_2(x)$, we generate to lowest order a term of the shape $U_{12} \int dx \Pi_1(x) \Pi_2(x)$, but in addition an infinite number of nonlinear terms, corresponding to all harmonics in the representation. However, only the terms for which the linear terms ($2\pi m_{1/2} v_{1/2} x$) cancel can drive a phase transition. For a continuous system this happens for $m_1 v_1 - m_2 v_2 = 0$, whereas for a system on a lattice, we have the condition $m_1 v_1 - m_2 v_2 = m_3$, where m_1 , m_2 , and m_3 are integer numbers. In general, higher integer numbers correspond to terms that are less relevant, because the scaling dimension of the nonlinear term scales quadratically with these integers. We are therefore led to consider small integer ratios between the fillings and the lattice if present. In Mathey and Wang (2007), we considered two cases of commensurabilities: a Mott insulator transition coupled to an incommensurate liquid and a fermionic liquid at half-filling coupled to an incommensurate bosonic liquid. In both cases the commensurability occurs between one species and the lattice, but does not involve the second species. Here, we consider the two most relevant, i.e., lowest order, cases which exhibit a commensurability that involves both species. The first case is the case of equal filling $v_1 = v_2$; the second is the case of the total density being unity, i.e., $v_1 + v_2 = 1$, where the densities v_1 and v_2 themselves are incommensurate. The first case can drive the system to a spin-gapped state, the second to a charge gapped state. We will determine in which parameter regime these transitions occur and what type of QRLO the

system exhibits in the vicinity of the transition. These two cases can be mapped onto each other via a dual mapping, which enables us to study only one case and then infer the results for the second by using this mapping. We will write out our discussion for the case of equal filling and merely state the corresponding results for complementary filling.

The action of a two-species mixture with equal filling in bosonized form is given by

$$S = S_{0,1} + S_{0,2} + S_{12} + S_{\text{int}}. \quad (6)$$

The terms $S_{0,j}$, with $j = 1, 2$, are given by

$$S_{0,j} = \frac{1}{2\pi K_j} \int d^2r \left(\frac{1}{v_j} (\partial_\tau \theta_j)^2 + v_j (\partial_x \theta_j)^2 \right). \quad (7)$$

Each of the two types of atoms, regardless of being bosonic or fermionic, is characterized by a Luttinger parameter $K_{1/2}$ and a velocity $v_{1/2}$. Here we integrate over $\mathbf{r} = (v_0 \tau, x)$, where we defined the energy scale $v_0 = (v_1 + v_2)/2$. The term S_{12} describes the acoustic coupling between the two species, and is bilinear:

$$S_{12} = \frac{U_{12}}{\pi^2} \int d^2r \partial_x \theta_1 \partial_x \theta_2 + \frac{V_{12}}{\pi^2} \int d^2r \partial_\tau \theta_1 \partial_\tau \theta_2. \quad (8)$$

The second term is created during the RG flow; its prefactor therefore has the initial value $V_{12}(0) = 0$. We define $S_0 = S_{0,1} + S_{0,2} + S_{12}$, which is the diagonalizable part of the action. S_{int} corresponds to the non-linear coupling between the two liquids, which we study within an RG approach:

$$S_{\text{int}} = \frac{2g_{12}}{(2\pi\alpha)^2} \int d^2r \cos(2\theta_1 + 2\theta_2). \quad (9)$$

This bosonized description applies to a BBM, a BFM, and a FFM. Depending on which of these mixtures we want to describe, we construct either bosonic or fermionic operators according to Haldane's construction (Cazalilla 2004; Haldane 1981):

$$f/b = [v_0 + \Pi]^{1/2} \sum_{m \text{ odd/even}} e^{mi\Theta} e^{i\Phi}. \quad (10)$$

v_0 is the zero mode of the density and $\Phi(x)$ is the phase field, which is the conjugate field of the density fluctuations $\Pi(x)$. The action for a mixture with complementary filling, $v_1 + v_2 = 1$, is of the form $S_0 + S_{\text{int}}'$, where the interaction S_{int}' is given by

$$S'_{\text{int}} = \frac{2g_{12}}{(2\pi\alpha)^2} \int d^2r \cos(2\theta_1 + 2\theta_2). \quad (11)$$

To map the action in Eq. 6 onto this system, we use the mapping $\theta_2 \rightarrow -\theta_2$, $\phi_2 \rightarrow -\phi_2$, and $g_{12} \rightarrow -g_{12}$, which evidently maps a mixture with complementary filling and attractive (repulsive) interaction and onto a mixture with equal filling with repulsive (attractive) interaction.

To study the action given in Eq. 6, we perform an RG calculation along the lines of the treatment of the sine-Gordon model in Gogolin et al. (1998) and Kogut (1979). In our model, a crucial modification arises: The linear combination $\theta_1 - \theta_2$ that appears in the nonlinear term is not proportional to an eigenmode of S_0 , and therefore, the RG flow does not affect only one separate sector of the system, as in an SU(2)-symmetric system. The RG scheme that we use here proceeds as follows: First, we diagonalize S_0 through the transformation (see Mathey 2007) $\theta_2 = B_1\tilde{\theta}_1 + B_2\tilde{\theta}_2$ and $\theta_1 = D_1\tilde{\theta}_1 + D_2\tilde{\theta}_2$, where $B_{1/2}$ and $D_{1/2}$ are some coefficients, and $\tilde{\theta}_{1/2}$ are the eigenmode fields with velocities $\tilde{v}_{1/2}$. Now we introduce an energy cutoff Λ on $\tilde{\theta}_{1/2}$ according to $\omega^2/\tilde{v}_{1/2} + \tilde{v}_{1/2}k^2 < \Lambda^2$. We shift this cutoff by an amount $d\Lambda$ and correct for this shift up to second order in g_{12} . At first order, only g_{12} is affected; its flow equation is given by

$$\frac{dg_{12}}{dl} = \left(2 - K_1 - K_2 - \frac{2}{\pi} \frac{U_{12} + V_{12}v_1v_2}{v_1 + v_2} \right) g_{12}, \quad (12)$$

with $d_l = d\Lambda/\Lambda$. At second order several terms are created that are quadratic in the original fields θ_1 and θ_2 . We undo the diagonalization and absorb

these terms into the parameters of the action, which concludes the RG step. By iterating this procedure we obtain these flow equations at second order in g_{12} :

$$\frac{dK_{1/2}}{dl} = -\frac{g_{12}^2}{16\pi^2} \left(2 + \left(\frac{v_2}{v_1} + \frac{v_1}{v_2} \right) \right), \quad (13)$$

$$\frac{dv_1}{dl} = v_1 \frac{g_{12}^2}{16\pi^2} \left(\frac{v_2}{v_1} - \frac{v_1}{v_2} \right), \quad (14)$$

$$\frac{dv_2}{dl} = v_2 \frac{g_{12}^2}{16\pi^2} \left(\frac{v_1}{v_2} - \frac{v_2}{v_1} \right), \quad (15)$$

$$\frac{dU_{12}}{dl} = -\frac{g_{12}^2}{8\pi} (v_1 + v_2), \quad (16)$$

$$\frac{dV_{12}}{dl} = -\frac{g_{12}^2}{8\pi} (1/v_1 + 1/v_2). \quad (17)$$

The system of differential equations, Eqs. 12–17, can show two types of qualitative behavior: The coefficient g_{12} of the nonlinear term (9) can either flow to zero, i.e., S_{int} is irrelevant, or it diverges, leading to the formation of an energy gap. In the first case, the system flows to a fixed point that is described by a renormalized diagonalizable action of the type S_0 , from which the quasi-phases can be determined.

When S_{int} is relevant, we introduce the fields (Voit 1995) $\theta_{\rho/\sigma} = \frac{1}{\sqrt{2}}(\theta_1 \pm \theta_2)$, which define the charge and the spin sector of the system. In this regime, these sectors decouple. Each of the two sectors is characterized by a Luttinger parameter and a velocity, $K_{\rho/\sigma}$ and $v_{\rho/\sigma}$, which are related to the original parameters in S_0 in a straightforward way. Using the numerical solution of the flow equations, we find that $K_\sigma \rightarrow 0$, as can be expected for an ordering of the nature of a spin gap, leaving K_ρ the only parameter characterizing the QLRO in this phase.

In order to determine the QLRO in the system, we will determine the scaling exponents of various order parameters. The order parameter with the largest positive scaling exponent shows the dominant order, whereas other orders with positive exponent are subdominant.

We will now apply this procedure to the different types of mixtures. For a FFM we find that the system always develops a gap, with the exception of the repulsive SU(2) symmetric regime (cf. Cazalilla et al. 2005). To determine the QLRO we introduce the following operators (Giamarchi 2004; Voit 1995):

$$\begin{aligned} O_{SS} &= \sum_{\sigma, \sigma'} \tilde{\sigma} f_{R, \sigma} \delta_{\sigma, \sigma'} f_{L, 3-\sigma'}, \\ O_{TS}^a &= \sum_{\sigma, \sigma'} \tilde{\sigma} f_{R, \sigma} \sigma_{\sigma, \sigma'}^a f_{L, 3-\sigma'}, \\ O_{CDW} &= \sum_{\sigma, \sigma'} f_{R, \sigma}^\dagger \delta_{\sigma, \sigma'} f_{L, \sigma'}, \quad \text{and} \\ O_{SDW}^a &= \sum_{\sigma, \sigma'} \tilde{\sigma} f_{R, \sigma}^\dagger \sigma_{\sigma, \sigma'}^a f_{L, \sigma'}, \end{aligned}$$

with $\sigma, \sigma' = 1, 2$, $\tilde{\sigma} = 3 - 2\sigma$, and $a = x, y, z$. In the gapless SU(2) symmetric regime, both CDW and SDW show QLRO, with both scaling exponents of the form $\alpha_{SDW/CDW} = 1 - K_p$ (Voit 1995), which shows that these orders are algebraically degenerate. Within the gaped regime the scaling exponents of these operators are given by $\alpha_{SS, TSz} = 2 - K_p^{-1}$ and $\alpha_{CDW, SDWz} = 2 - K_p$. As discussed in Giamarchi (2004), the sign of g_{12} determines whether CDW or SDW_z and SS or TS_z appear. In Fig. 4a, we show the phase diagram based on these results. In addition to these phases, we indicate the appearance of the Wentzel-Bardeen instability, shown as phase separation for repulsive interaction and collapse for attractive interaction.

We will now use the dual mapping to obtain the phase diagram of a FFM with complementary filling from Fig. 4a. Under this mapping, the attractive and repulsive regimes are exchanged with the following replacements: CDW $\rightarrow$ SDW_z, SDW_z $\rightarrow$ CDW, SS, TS_z $\rightarrow$ SDW, and SDW $\rightarrow$ SS. Note that the gapless regime is now on the attractive side, with degenerate CDW and SS pairing.

For BBMs we proceed in the same way as for FFMs. We introduce the following set of order parameters: $O_{CDW} = b_1^\dagger b_1 + b_2^\dagger b_2$, $O_{SS} = b_1 b_2$, $O_{SDW_z} = b_1^\dagger b_1 + b_2^\dagger b_2$, $O_{SDW_x} = b_1^\dagger b_2 + b_2^\dagger b_1$, $O_{SDW_y} = -i(b_1^\dagger b_2 - b_2^\dagger b_1)$, and in addition the

superfluid (SF) order parameters b_1 and b_2 . In Fig. 4a we show the phase diagram of a mixture of a BBM of hardcore bosons, which is almost identical to the one of a FFM. The phase diagram of the mixture with complementary filling, as obtained from the dual mapping, is also of the same form as its fermionic equivalent, with the exception of the gapless regime, in which BBMs show supersolid behavior (coexistence of SF and CDW order), and with the replacement TS_z $\rightarrow$ SS.

In Fig. 5b, we show the phase diagram of a mixture of hardcore bosons (species 1) and bosons in the intermediate to hardcore regime (species 2). If species 2 is sufficiently far away from the hardcore limit, the system remains gapless. However, in the vicinity of the transition, the scaling exponents of the liquids are affected by the RG flow. As indicated, the effective scaling exponent of the hardcore bosons is renormalized to a value that is smaller than 1, and therefore, we find both SF and CDW order, i.e., supersolid behavior. The phase diagram of the dual mixture is of the following form: The attractive and the repulsive regimes are exchanged, and in the gaped phase, we again have the following mapping: CDW $\rightarrow$ SDW_z, SDW_z $\rightarrow$ CDW, SS $\rightarrow$ SDW, and SDW $\rightarrow$ SS. The gapless regime is unaffected.

For a BFM we find that the order parameters O_{CDW} , O_{SDW_z} , $O_{f-PP} = f_R f_L e^{-2i\lambda\Phi_b}$ (Mathey et al. 2004; Mathey and Wang 2007), and b can develop QLRO in the gapless regime. In the gaped regime, the order parameters $O_{PP} \equiv f_R b f_L b$ and $O_{PP'} \equiv f_R b^\dagger f_L b^\dagger$, in addition to O_{CDW} , show QLRO. ($O_{PP/PP'}$ are special cases of the polaron pairing operators discussed in Mathey et al. (2004), and Mathey and Wang (2007).) In Fig. 4b we show the phase diagram of a BFM with hardcore bosons, and in Fig. 5a, we vary the Luttinger parameter of the bosons. In both the gapless phase and the gaped phase, we find that CDW and f -PP or PP, respectively, are mutually exclusive and cover the entire phase diagram, cf. (Mathey et al. 2004; Mathey and Wang 2007). The dual mapping again maps attractive and repulsive regimes onto each other. Within the gaped phase we find the mapping CDW $\rightarrow$ SDW_z, SDW_z $\rightarrow$ CDW, and PP $\rightarrow$ PP'; the gapless regime is unaffected.

Before we conclude, we discuss how these predictions could be measured experimentally. CDW order will create additional peaks in TOF images, corresponding to a wavevector $Q = 2k_F$. As demonstrated and pointed out in Altman et al. (2004), Fölling et al. (2005), Greiner et al. (2005), and Mathey et al. (2008a), the noise in TOF images allows to identify the different regimes of both gaped and gapless phases. As discussed in Mathey et al. (2004) and Mathey and Wang (2007), a laser stirring experiment could determine the onset of CDW order for fermions or the supersolid regime for bosons. RF spectroscopy (Chin et al. 2004) can be used to determine the presence and the size of an energy gap.

In conclusion, we have studied mixtures of ultracold atoms in 1D with commensurate filling. We used a Luttinger liquid description which enables us to study FFMs, BFMs, and BBMs in a single approach. We find that FFMs are generically gaped for both attractive and repulsive interactions, whereas for BFMs and BBMs the bosons need to be close to the hardcore limit. We find a rich structure of quasi-phases in the vicinity of these transitions, in particular a supersolid phase for BBMs that occurs close to the hardcore limit. Experimental methods to detect the predictions were also discussed.

Phase-Locking Transition of Coupled Low-Dimensional Superfluids

Most phase transitions that have been realized in ultracold atom systems are generic first- or second-order transitions. However, the paradigm of phase transitions in two dimensions at finite temperature is of a more intricate type, a Kosterlitz-Thouless transition, which is characterized by a change of the functional form of the correlation function of the order parameter, from algebraic decay to exponential decay. In an intriguing new development in studying low-dimensional strongly correlated systems, such a Kosterlitz-Thouless (KT) transition (Chaikin and Lubensky 1995) was indeed realized and observed (Hadzibabic et al. 2006). In this experiment the interference amplitude between two

independent two-dimensional (2D) Bose systems was studied as a function of temperature. This analysis revealed the jump in the superfluid stiffness (see also Polkovnikov et al. 2006) and the emergence of unpaired isolated vortices as they crossed the phase transition.

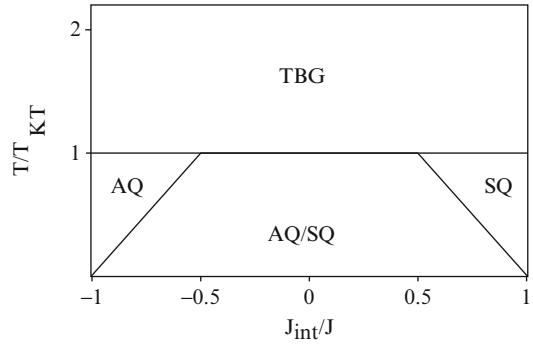
The other focus of this section, the physics of ramping across a phase transition, is also triggered by a recent experiment: Sadler et al. observed spontaneous generation of topological defects in the spinor condensate after a sudden quench (i.e., a rapid, non-adiabatic ramp) through a quantum phase transition (Sadler et al. 2006). A similar experiment in a double-layer system was reported in Scherer et al. (2006). The topological defects are generated (Kibble 1976) at a density which is related to the rate at which the transition is crossed (Zurek 1985). Later it was argued that the dependence of the number of such defects on the swipe rate across a quantum critical point can be used as a probe of the critical exponents characterizing the phase transition (Polkovnikov 2005; Zurek et al. 2005; Dziarmaga 2005). This Kibble-Zurek (KZ) mechanism was originally considered as an early universe scenario creating cosmic strings, which would serve as an ingredient for the formation of galaxies. (Since then, it has been established that cosmic strings can only contribute a small fraction of the initial density perturbations. We thank T. Kibble for this comment.) Cold atom systems appear to be a very suitable laboratory for performing such “cosmological experiments,” since these systems are highly tunable and well isolated from the environment. So far the experiments and the theoretical proposals addressed the KZ scenario across a quantum phase transition. The main reason is that it is generally hard to cool such systems sufficiently fast to observe non-equilibrium effects. In this work we provide an example of a particular system where this difficulty can be easily overcome by quenching the transition temperature T_c instead of T . Thus, the relevant ratio T/T_c can be tuned with an arbitrary rate and the KZ mechanism can be observed. Specifically, we examine a system of two superfluids (SF): As we show below, by turning on tunneling between the two systems, the transition temperature increases rapidly, and the system

attempts to create long-range order (LRO). However, in this process, defects in the SF phase are created, which develop into long-lived vortex-antivortex pairs or in finite system unbalanced population between vortices and antivortices. We note that because the systems are isolated and there is no external heat bath, the temperature itself also changes due to the quench. However, the long-wavelength fluctuations relevant for the KT transition are only a small subset of all degrees of freedom, majority of which are only weakly affected by small interlayer tunneling. So we believe that the change of the T_c is the main effect of the quench.

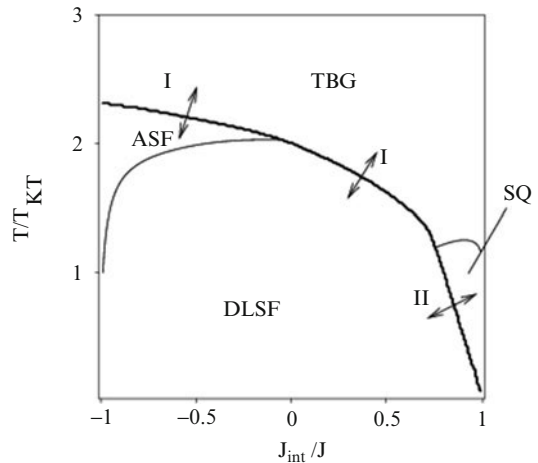
In this section we consider two SFs coupled via tunneling and/or interactions. In the experiments the hopping or tunneling rate between two systems can be tuned to a high precision (Hadzibabic et al. 2006, 2004; Paredes et al. 2004; Schumm et al. 2005). Interactions between the atoms in different systems can either be realized in ensembles of polar molecules or by using mixtures of two hyperfine states, where the tunneling rate is controlled by an infrared light source (Jo et al. 2007), which induces spin-flipping between the hyperfine states. In this case the atoms in different states naturally interact with each other since they are not physically separated in space. The main results of our analysis are the phase diagrams of coupled SFs in Figs. 6 and 7, the behavior of T_c , and the energy gap shown in Fig. 8, as well as the proposal of realizing the KZ mechanism by switching on the tunneling between two SFs.

2D Superfluids

In this section we consider two 2D SFs, each characterized by a KT temperature T_{KT} . We write the bosonic operators $b_{1/2}$ in the two layers in a phase-density representation (Chaikin and Lubensky 1995; Gogolin et al. 1998), $b_{1/2} \sim \sqrt{\rho_{1/2}} \exp(i\phi_{1/2})$, where $\rho_{1/2}$ are the density operators of the two systems and $\phi_{1/2}$ the phases. The low-momentum fluctuations of the phase fields are described by Gaussian contributions to the Hamiltonian $\mathcal{H}_0$. Because of the formal analogy between the quantum 1D and thermal



Ultracold Atomic Gases: Novel States of Matter, Fig. 6 Phase diagrams of two 2D SFs, coupled through a term of the form $S_{12} S_{12}$, Eq. 22, in terms of J_{int}/J and T/T_{KT} . For low temperatures we find antisymmetric quasi-order (AQ) and/or symmetric quasi-order (SQ), which undergo a KT transition either simultaneously due to single vortices (AQ/SQ to thermal Bose gas (TBG) phase) or individually due to correlated vortex pairs: Symmetric (antisymmetric) vortex pairs drive the AQ/SQ to AQ (SQ) transition

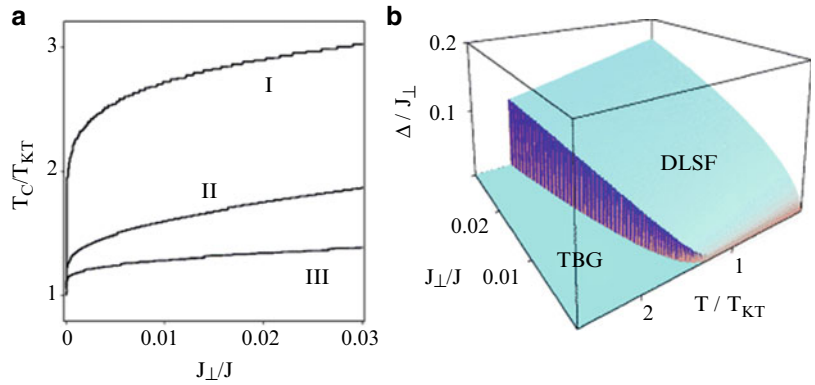


Ultracold Atomic Gases: Novel States of Matter, Fig. 7 Phase diagram, temperature (in units of T_{KT}) versus interaction (in units of J). We assume $J_{\perp}/J \sim 10^{-3}$ and $A_1/J \sim 10^{-3}$. DLSF double-layer superfluid, TBG thermal Bose gas, ASF antisymmetric superfluid, SQ symmetric quasi-order. The order of the transition lines are either first order (I), second order (II), or KT (thin lines)

2D systems (Giamarchi 2004), we adopt the quantum terminology throughout the paper and refer to the ratio of the Hamiltonian and the temperature as the action. Then

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Fig. 8 (a) Critical temperature T_c of the DLSF-TBG transition (in units of T_{KT}) for different values of A_1/J : 10^{-3} , 0.1, 0.4 (I–III) and for $J_{int} = 0$. (b) Energy gap in the anti-symmetric sector (in units of $J_\perp$) as a function of $J_\perp/J$ and temperature (in units of T_{KT}). We have set $A_1/J = 0.1$ and $J_{int} = 0$



$$S_0 \equiv \frac{\mathcal{H}_0}{T} = \frac{J}{2T} \int d^2r \left[(\nabla\phi_1)^2 + (\nabla\phi_2)^2 \right]. \quad (18)$$

The energy scale J here is related to T_{KT} by $J = 2T_{KT}/\pi$. Besides these long-wavelength fluctuations, the system also contains additional degrees of freedom, vortex-antivortex pairs (Chaikin and Lubensky 1995). The corresponding term in the action is expressed through the dual fields $\theta_{1,2}$ (Gogolin et al. 1998):

$$S_1 = \frac{2A_1}{T} \int \frac{d^2r}{(2\pi\alpha)^2} [\cos(2\theta_1) + \cos(2\theta_2)], \quad (19)$$

where α is a short-distance cutoff of the size of the vortex core and A_1 is proportional to the single-vortex fugacity, $A_1 \sim J \exp(-J/T)$, where we assume both SFs to have the same effective parameters J and A_1 . Operators of the type $\exp(2i\theta)$ create kinks in the field ϕ : $\exp(-2i\theta(x))\phi(x')\exp(2i\theta(x)) \sim \phi(x') + 2\pi\Theta(x - x')$, $\Theta(x)$ being the step function, which corresponds to the effect of vortices in the original 2D problem (Giamarchi 2004, p. 92).

In addition, the two systems are coupled by a hopping term $\sim t_\perp b_1^\dagger b_2 + \text{h.c.}$, which results in the following contribution to the action:

$$S_\perp = \frac{2J_\perp}{T} \int \frac{d^2r}{(2\pi\alpha)^2} \cos(\phi_1 - \phi_2), \quad (20)$$

where the bare value of $J_\perp$ corresponds approximately to $t_\perp\rho_0$. In principle, the hopping term is

modified by the vortex contributions; however, these corrections are always irrelevant under renormalization group (RG).

For most of the discussion in this entry, we use the symmetric and antisymmetric combinations of $\phi_{1/2}$ and $\theta_{1/2}$:

$$\phi_{s/a} = (\phi_1 \pm \phi_2)/\sqrt{2}, \quad \theta_{s/a} = (\theta_1 \pm \theta_2)/\sqrt{2}. \quad (21)$$

Written in these fields, the term S_0 in Eq. 18 is again a sum of Gaussian models, now in the fields ϕ_s and ϕ_a , with the same energy scale J . However, we will consider a broader class of actions, in which the energy scales of the symmetric and antisymmetric sectors differ. We include the following term in the action:

$$S_{12} = \frac{J_{int}}{T} \int d^2r \nabla\phi_1 \nabla\phi_2. \quad (22)$$

With this, the quadratic part of the action is given by

$$S_0 + S_{12} = \frac{J_s}{2T} \int d^2r (\nabla\phi_s)^2 + \frac{J_a}{2T} \int d^2r (\nabla\phi_a)^2, \quad (23)$$

where J_s and J_a are given by $J_{s/a} = J \pm J_{int}$.

We now motivate the existence of such a term S_{12} in ultracold atom systems, by considering two BECs coupled by a short-range density-density interaction. Starting from a Hamiltonian of the

form $H = \sum_{\mathbf{k}} \left[\epsilon_{\mathbf{k}} b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + (g/2V) \rho_{\mathbf{k}}^\dagger \rho_{\mathbf{k}} \right]$, where $b_{\mathbf{k}}$

is the boson operator, $\epsilon_{\mathbf{k}}$ is the free dispersion $\epsilon_{\mathbf{k}} = \mathbf{k}^2/2m$, g is the interaction strength of the contact interaction, V is the volume, and $\rho_{\mathbf{k}}$ is the density operator of momentum $\mathbf{k}$, given by $\rho_{\mathbf{k}} = \sum_{\mathbf{p}} b_{\mathbf{p}}^\dagger b_{\mathbf{p}+\mathbf{k}}$, we assume that the zero

momentum mode is macroscopically occupied and formally replace the operator b_0 by a number, $b_0 \rightarrow \sqrt{N_0}$, where N_0 is the number of condensed atoms which is comparable to the total atom number N , i.e., $N_0 \sim N$. Next we keep all terms that are quadratic in $b_{\mathbf{k}}$ (with $\mathbf{k} \neq 0$) and perform a Bogoliubov transformation, given by $b_{\mathbf{k}} = u_{\mathbf{k}} \beta_{\mathbf{k}} + v_{\mathbf{k}} \beta_{-\mathbf{k}}^\dagger$, to diagonalize the Hamiltonian. The eigenmodes $\beta_{\mathbf{k}}$ have a dispersion relation $\omega_{\mathbf{k}} = \sqrt{\epsilon_{\mathbf{k}}(\epsilon_{\mathbf{k}} + 2gn)}$, with n being the density N/V . The low- $\mathbf{k}$ limit is given by $\omega_{\mathbf{k}}^2 \sim v^2 |\mathbf{k}|^2$, with $v = \sqrt{gn/m}$, which corresponds to the contribution in Eq. 18 of the action. Next, we consider the sum of two copies of the previous Hamiltonian with boson operators $b_{1/2}$. In addition we consider an interaction $H_{12} = g_{12}/V \sum_{\mathbf{k}} \rho_{1,\mathbf{k}}^\dagger \rho_{2,\mathbf{k}}$, where the density operators $\rho_{1/2,\mathbf{k}}$ are given by $\rho_{1/2,\mathbf{k}} = \sum_{\mathbf{p}} b_{1/2,\mathbf{p}}^\dagger b_{1/2,\mathbf{p}+\mathbf{k}}$. Following the same

procedure as before, we find two eigenmode branches, corresponding to inphase and out-of-phase superpositions of the modes of each condensate, with the dispersions $\omega_{s/a,\mathbf{k}}^2 \sim v_{s/a}^2 |\mathbf{k}|^2$, with the velocities $v_{s/a} = \sqrt{(g \pm g_{12})n/m}$. Therefore, for this example, the energy scale J_{int} is related to $g_{12}n/m$, which would be of similar order as J for a system interacting via contact interaction, for small temperatures. This discussion only applies to the weakly interacting limit of a true condensate. However, it demonstrates that a density-density contact interaction term can lead to a substantial energy splitting of the inphase and out-of-phase modes.

Finally, in addition to single vortices in each SF, we have to consider the possibility of correlated vortex pairs, i.e., one vortex in each layer at the same location of either the same or of opposite vorticity. We will refer to these vortex configurations as *symmetric* or *antisymmetric vortex pairs*, respectively. These excitations appear as the following terms in the action:

$$S_{s,a} = \frac{2A_{s,a}}{T} \int \frac{d^2 r}{(2\pi\alpha)^2} \cos \left(2\sqrt{2}\theta_{s,a} \right). \quad (24)$$

These correlated vortex terms, which describe new degrees of freedom, can be the most relevant nonlinear terms in the action, which derives from the possibility that the vortices in different layers interact with each other, through the terms (20) and (22). The effect of these terms is the following: At low temperatures the energy between two single vortices of opposite vorticity due to tunneling grows as the square of the distance D between them, i.e., as $J_{\perp}(D/\alpha)^2$. As a result, the tunneling term attempts to confine vortices of opposite vorticity, leading to phase-locking between the layers, which we describe further later on. The interaction S_{12} changes the energy of correlated vortex pairs as follows: The energy of a single vortex is given by $2\pi J \log L/\alpha$, where L is the system size, whereas a symmetric/antisymmetric vortex pair has an energy of $4\pi(J \pm J_{\text{int}}) \log L/\alpha$. Therefore, symmetric vortex pairs are the lowest energy vortex excitations for $J_{\text{int}} < -J/2$, whereas for $J_{\text{int}} > J/2$, antisymmetric vortex pairs are the lowest energy excitations. As we will see below, in these regimes correlated vortex pairs drive transitions to phases, in which one sector is (quasi-)SF, whereas the other is disordered. We will also see that these terms are generated under the RG flow, even if not present at the onset.

We note that a similar system has been studied in Casalilla (2004). Here, we consider a larger class of systems by including the interaction term (22), which in turn requires us to include the correlated vortex excitations (Eq. 24). These terms give rise to additional phases as we will see in the following.

Next we analyze our system within the RG approach. This RG flow is perturbative in the vortex fugacities A_1 , A_s , and A_a and the tunneling energy $J_{\perp}$ and therefore applies to the weak-coupling limit (in particular $J_{\perp} \rightarrow +0$). At second order the flow equations are given by Benfatto et al. (2007):

$$\frac{dJ_{\perp}}{dl} = \left(2 - \frac{T}{2\pi J_a}\right) J_{\perp}, \quad (25)$$

$$\frac{dA_s}{dl} = \left(2 - 2\pi \frac{J_s}{T}\right) A_s + \alpha_3 \frac{A_1^2 (J_a - J_s)}{2T^2}, \quad (26)$$

$$\frac{dA_a}{dl} = \left(2 - 2\pi \frac{J_a}{T}\right) A_a + \alpha_3 \frac{A_1^2 (J_s - J_a)}{2T^2}, \quad (27)$$

$$\frac{dA_1}{dl} = \left(2 - \frac{\pi(J_s + J_a)}{2T} + \alpha_3 \frac{A_s J_s + A_a J_a}{T^2}\right) A_1, \quad (28)$$

$$\frac{dJ_a}{dl} = \alpha_2 \left(\frac{J_1^2}{4\pi^4 J_a} - 4 \frac{A_a^2}{T^4} J_a^3 - \frac{A_1^2}{2T^4} (J_s + J_a) J_a^2 \right), \quad (29)$$

$$\frac{dJ_s}{dl} = -\alpha_2 \left(2 \frac{A_s^2}{T^4} J_s^2 + \frac{A_1^2}{4T^4} (J_s + J_a) J_s \right) 2J_s. \quad (30)$$

The coefficients $\alpha_{2/3}$ are non-universal parameters that appear in the RG procedure (Kogut 1979), and which do not affect the results qualitatively. For consistency, we have to expand the right-hand side of the above equations up to second order, around the resulting Gaussian fixed point : $J_{s/a} = J \pm J_{\text{int}} + j_{s/a}$. We emphasize again that J_{int} near the fixed point can be generated by RG and be nonzero even if it is not present at the onset.

Before we consider the full RG flow, we consider the simpler case of no tunneling, i.e., we solve the RG equations while setting $J_{\perp} = 0$. In Fig. 6 we show the phase diagram of two 2D SFs coupled by S_{12} , Eq. 22. Such a system would be realized by a 2D mixture of bosonic atoms in two different hyperfine states, interacting via some short-range potential. The order parameters we consider are $O_s(x) = b_1(x)b_2(x)$ and $O_a(x) = b_1^{\dagger}(x)b_2(x)$. To obtain the phase diagram, we consider the correlation functions of each of these order parameters, which can either scale algebraically or exponentially. In Fig. 6 we refer to algebraic scaling of $O_s(x)$ as symmetric quasi-order (SQ) and of $O_a(x)$ as anti-symmetric quasi-order

(AQ). In each of the sectors, a KT transition marks the transition from the algebraic to the exponential regime, which occur either simultaneously and are driven by single-vortex excitations or at different temperatures and are driven by correlated vortex pairs. As a result we find four regimes: At temperatures above T_{KT} , both sectors are disordered, giving rise to a thermal Bose gas (TBG) phase. For temperatures below T_{KT} , and for a wide range of J_{int} , we find that both sectors are quasi-SF (AQ/SQ), which is the only phase in which the correlation function of the single boson operators shows algebraic scaling. We also find regimes in which only one sector shows algebraic scaling, whereas the other is disordered (AQ and SQ). From the perspective of vortices, the TBG phase is a gas of free single vortices in each layer, whereas the AQ (SQ) phase is a gas of symmetric (antisymmetric) vortex pairs.

We now consider the full RG system, including $J_{\perp}$. We numerically integrate the RG equations, and find the phase diagram shown in Fig. 7 in terms of the temperature T and the interaction J_{int} . We again find four different phases that are different combinations of LRO, QLRO, and disorder in the symmetric and anti-symmetric sector. At high temperatures we find that both sectors are disordered in a TBG phase, as before. For lower temperatures and for a wide range of J_{int} , the system is in a double-layer SF phase (DLSF): The symmetric sector shows algebraic scaling, whereas the exponent of the anti-symmetric sector is renormalized to zero, i.e., we find two SFs that are phase-locked due to $J_{\perp}$. Note that the transition temperature T_c between DLSF and TBG has been noticeably increased relative to the decoupled value T_{KT} , as we will discuss further later on. We also find two additional phases, which are partially (quasi-)SF and partially disordered. One of them is the SQ phase, as before, whereas the other one (ASF) now shows true LRO in the antisymmetric sector due to $J_{\perp}$, whereas the symmetric sector remains disordered. We note that the generic double-layer action that we discuss in this entry does not show a sliding phase (Mukhopadhyay et al. 2001), for any nonzero $J_{\perp}$.

Either S_1 or S_a , which is generated by RG, drives the anti-symmetric sector to a disordered state, or $S_\perp$ creates true LRO in the field ϕ_a .

We also use the RG flow to find the order of the phase transitions in the weak-coupling limit that the anti-symmetric sector undergoes, by determining the energy gap using a “poor man’s scaling” argument: When the coupling amplitude $J_\perp(l^*)$ is of order unity, the corresponding gap is given by the expression $\Delta \sim J_\perp \exp(-l^*)$. From the behavior of Δ at the phase transition, we can read off whether it is of first or second order, as indicated in Fig. 7.

Given the nature of an effective theory, only approximate statements can be made about how the different regimes of the phase diagram relate to the microscopic interactions. To create the ASF or AQ phase, an attraction between the two atom species is needed that is of order J , whereas to create the SQ phase, a repulsion of that order would be needed. To detect the different phases, one could use the interference method used in Hadzibabic et al. (2006) to distinguish the phase-locked phases (DLSF and ASF), which would show a well-defined interference pattern, from the uncorrelated phases. Another approach would be time-of-flight images: The DLSF phase would display a quasi-condensate signature, whereas the other phases would appear disordered. However, at the transition from ASF or SQ to TBG, the width of the distribution would abruptly increase.

Kibble-Zurek Mechanism

In this section we discuss how the phase-locking transition found in the previous section could be used to realize the KZ mechanism. The defining property of this mechanism is the generation of topological defects by ramping across a phase transition, coming from the disordered phase. The disordered phase that we propose to use is the TBG phase of the *decoupled* 2D systems, that is, we consider the experimental setup reported in Hadzibabic et al. (2006) for a temperature T above the KT temperature T_{KT} . The ordered phase we consider is the DLSF phase, i.e., the phase-locked phase of two *coupled* SFs. The ramping is achieved by turning on the tunneling between the two layers, which can be done by lowering the potential barrier

between them. For this procedure the critical temperature T_c of the DLSF-TBG transition needs to be above the KT temperature of the uncoupled systems. We now show that the RG flow indeed predicts such a scenario. In the experiments in Hadzibabic et al. (2006), the atoms in different layers do not interact with each other. Therefore, it can be expected that J_{int} is small, of order $J_\perp$, which motivates us to discuss the case $J_{\text{int}} = 0$ here. We note, however, that the desired scenario of an increased critical temperature is found for a wide range of J_{int} , as can be seen in Fig. 7. In Fig. 8a we show how the critical temperature of the DLSF-TBG transition behaves, predicted by the RG flow, for different values of A_1 . The critical temperature shows a sizable increase, due to the phase-locking transition. Due to the perturbative nature of the RG scheme, the RG flow underestimates the effects of the term S_1 and predicts a finite jump of the critical temperature when $J_\perp$ is turned on. However, to lock the SFs together in the regime slightly above T_{KT} , $J_\perp$ needs to be at least of the order of the vortex core energy, giving rise to a finite slope of T_c instead of a jump. The energy gap of this transition is shown in Fig. 8 from which we can see that the transition is of first order, in contrast to the second-order transition described in Kibble (1976) and Zurek (1985), which is advantageous because the onset of order is instantaneous rather than continuous. We note that the phase diagram was obtained using the assumption that the bare parameters of the model, in particular J , do not depend on temperature. This is true only if temperature is close to T_{KT} . Here we find that the ratio T_c/T_{KT} can be relatively large. In fact T_c/T_{KT} will be always smaller than that shown in Fig. 8a; however, qualitatively the behavior of T_c/T_{KT} as a function of $J_\perp$ should remain intact. We point out that our results can be generalized to a system of $N > 2$ coupled SFs. One finds that the SFs still show a strong tendency to phase lock together. As a result the critical temperature should approximately satisfy the equality $\pi J(T_c) N = 2T_c$. Thus, as N increases T_c approaches the mean-field critical temperature at which the stiffness J vanishes, and we recover the usual 3D result.

In finite size systems there is another constraint on the minimum value of $J_\perp$: We consider the free energy of a single vortex in the antisymmetric

field, $\phi_a \sim \arctan(x/y)$. For the decoupled system we get for the free energy (Kogut 1979): $F \sim 2(\pi J - 2T) \log L/\alpha$, where L is the system size. The coupling term gives a free energy contribution $F_\perp \sim J_\perp (L/\alpha)^2$. In the thermodynamic limit, $L \rightarrow \infty$, this term diverges faster than the others, which is consistent with our finding of LRO in the antisymmetric sector. For a finite system, comparing these terms gives the estimate $J_\perp \sim J \log(L/\alpha)/(L/\alpha)^2$, that is required for this order to develop. With a system size $L/\alpha \sim 10^2$, that would require $J_\perp \sim 10^{-3}J$, which, for the setup in Hadzibabic et al. (2006), would be around $10^2 s^{-1}$.

As an estimate of the number of domains that would be created, we follow the argument in Kibble (1976): The coherence scale of the DLSF phase is given by $(J/\Delta)^{1/2}\alpha$, which is the scale of a Klein-Gordon model with a kinetic energy scale J and a “mass term” with a prefactor Δ/α^2 . The domain size is then given by $(J/\Delta)\alpha^2$ and the number of domains by $\sim (\Delta/J)L^2/\alpha^2$. As we show in Fig. 8b for $J_\perp/J \approx 10^{-2}$, we find $\Delta/J_\perp \sim 10^{-1}$, and therefore, $J/\Delta \sim 10^3$. With $L/\alpha \sim 10^2$, we would get $N_{\text{dom}} \sim 10^1 - 10^2$, which would generate a similar number of vortices. We estimate the vortex-antivortex imbalance by considering the number of domains around the periphery of the system, which scales as L/ξ . If we imagine that the phase behaves like a random walk, the total phase mismatch, corresponding to the vortex-antivortex imbalance, will scale as $\sqrt{L/\xi} \sim N_{\text{dom}}^{1/4}$, which, for $L/\alpha \sim 10^2$, is of the order $10^0 - 10^1$.

In summary, we propose the following procedure: (i) Prepare two uncoupled SFs at a temperature T slightly above T_{KT} . (ii) Switch on the tunneling between the two layers, which creates a DLSF phase with a critical temperature T_c higher than T . As a result, one should find a number of long-lived vortex-antivortex pairs in the antisymmetric phase field ϕ_a , which would be visible in an interference measurement, at a temperature where there would be none in thermal equilibrium.

In conclusion of the section, we studied the phase-locking transition of 2D superfluids, within a renormalization group approach. We find that this transition is accompanied by an increase of the transition temperature. We suggest that this

effect can be used to probe the Kibble-Zurek mechanism in cold atom systems by rapidly changing the ratio T/T_c . When we include interactions between the layers, we find additional phases, in which either the symmetric or the anti-symmetric sector is disordered, and the other sector stays superfluid or quasi-superfluid.

Bose-Fermi Mixtures in Two-Dimensional Optical Lattices

In the spirit of engineering many-body systems that are relevant in other fields, we now turn to atomic mixtures that resemble qualitatively, i.e., in terms of degrees of freedom of the system, electron-phonon systems. In two dimensions, these systems are actively studied and prove to be of considerable complexity. In order to study their atomic counterparts, Bose-Fermi mixtures in optical lattices, we use the powerful method of functional renormalization group equations, with which we can determine their phase diagrams in the weak-coupling limit in a systematic fashion. We find a rich competition of phases for both the square lattice and triangular lattice geometry that we consider.

In this section we consider mixtures of one bosonic type of atom and either two fermionic types that are SU(2) symmetric or spinless fermions. The Hamiltonian for a mixture on a square lattice is given by

$$\begin{aligned} H = & -t_f \sum_{\langle ij \rangle, s} f_{i,s}^\dagger f_{j,s} - t_b \sum_{\langle ij \rangle} b_i^\dagger b_j \\ & - \sum_i (\mu_f n_{f,i} + \mu_b n_{b,i}) \\ & + \sum_i \left[U_{ff} n_{f,i,\uparrow} n_{f,i,\downarrow} + \frac{U_{bb}}{2} n_{b,i} n_{b,i} + U_{bf} n_{b,i} n_{f,i} \right], \end{aligned} \quad (31)$$

where $f_{i,s}^\dagger$ ($f_{i,s}$) creates (annihilates) a fermion at site i with pseudo-spin s ($s = \uparrow, \downarrow$), $b_i^\dagger$ (b_i) creating (annihilates) a boson at site i , $n_{f,i} = \sum_s f_{i,s}^\dagger f_{i,s}$ ($n_{b,i} = b_i^\dagger b_i$) is the fermion (boson) number operator, t_f and t_b are the fermionic and bosonic tunneling

energies between neighboring sites, μ_f (μ_b) is the chemical potential for fermions (bosons), U_{bb} is the repulsion energy between bosons on the same site, U_{ff} is the repulsion energy between the two species of fermions, and U_{bf} is the repulsion energy between bosons and fermions. The two

fermion species have been treated as a pseudo-spin-1/2 index ($\uparrow$ and $\downarrow$). The case of spinless fermions can be immediately obtained from Eq. 31 by ignoring one of the spin states. In momentum space, the Hamiltonian Eq. 31 is written as

$$H = \sum_{\mathbf{k}} \left\{ (\epsilon_{f,\mathbf{k}} - \mu_f) \sum_s f_{\mathbf{k},s}^\dagger f_{\mathbf{k},s} + (\epsilon_{b,\mathbf{k}} - \mu_b) b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + \frac{U_{ff}}{V} \rho_{f,\mathbf{k},\uparrow} \rho_{f,-\mathbf{k},\downarrow} + \frac{U_{bb}}{2V} \rho_{b,\mathbf{k}} \rho_{b,-\mathbf{k}} + \frac{U_{bf}}{V} \rho_{b,\mathbf{k}} \rho_{f,-\mathbf{k}} \right\}, \quad (32)$$

where $\rho_{f,\mathbf{k}} = \sum_{\mathbf{q},s} f_{\mathbf{k}+\mathbf{q},s}^\dagger f_{\mathbf{k},s}$ ($\rho_{b,\mathbf{k}} = \sum_{\mathbf{q}} b_{\mathbf{k}+\mathbf{q}}^\dagger b_{\mathbf{k}}$) is the fermion (boson) density operator and $\epsilon_{b/f,\mathbf{k}} = -2t_{b/f} (\cos k_x + \cos k_y)$ is the bosonic/fermionic dispersion relation.

We consider the limit of weakly interacting bosons that form a BEC (Mathey et al. 2006; Wang et al. 2005), where we assume that the zero momentum bosonic mode is macroscopically occupied, and the corresponding operator b_0 can be formally replaced by a real number $b_0 \rightarrow \sqrt{N_0}$, where N_0 is the number of condensed atoms. After this replacement we keep all terms that are quadratic in $b_{\mathbf{k}}$ (with $\mathbf{k} \neq 0$) and perform a Bogoliubov transformation, given by $b_{\mathbf{k}} = u_{\mathbf{k}} \beta_{\mathbf{k}} + v_{\mathbf{k}} \beta_{-\mathbf{k}}^\dagger$, to diagonalize the bosonic Hamiltonian. The resulting eigenmodes $\beta_{\mathbf{k}}$ have a dispersion relation given by $\omega_{\mathbf{k}} = \sqrt{\epsilon_{b,\mathbf{k}}(\epsilon_{b,\mathbf{k}} + 2U_{bb}n_b)}$, with the low- $\mathbf{k}$ limit $\omega_{\mathbf{k}} \sim v_b |\mathbf{k}|$, with $v_b = \sqrt{2t_b U_{bb} n_b}$. The parameters $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ are given by $u_{\mathbf{k}}^2 = (\omega_{\mathbf{k}} + \epsilon_{b,\mathbf{k}} + U_{bb}n_b)/(2\omega_{\mathbf{k}})$ and $v_{\mathbf{k}}^2 = (-\omega_{\mathbf{k}} + \epsilon_{b,\mathbf{k}} + U_{bb}n_b)/(2\omega_{\mathbf{k}})$.

The density fluctuations of the bosons are approximated by $\rho_{b,\mathbf{k}} \approx \sqrt{N_0}(u_{\mathbf{k}} + v_{\mathbf{k}})(\beta_{\mathbf{k}} + \beta_{-\mathbf{k}}^\dagger)$, with $\mathbf{k} \neq 0$. The interaction between bosons and fermions is then given by $U_{bf} \sqrt{N_0}/V \sum_{\mathbf{k}} (u_{\mathbf{k}} + v_{\mathbf{k}})(\beta_{\mathbf{k}} + \beta_{-\mathbf{k}}^\dagger) \rho_{f,-\mathbf{k}}$. As a next step we integrate out the bosonic modes and use an instantaneous approximation, leading to the following effective Hamiltonian:

$$H_{\text{eff.}} = \sum_{\mathbf{k}} \left\{ (\epsilon_{\mathbf{k}} - \mu_f) \sum_s f_{\mathbf{k},s}^\dagger f_{\mathbf{k},s} + \frac{U_{ff}}{V} \rho_{f,\mathbf{k},\uparrow} \rho_{f,-\mathbf{k},\downarrow} + \frac{1}{2V} V_{\text{ind.},\mathbf{k}} \rho_{f,\mathbf{k}} \rho_{f,-\mathbf{k}} \right\}, \quad (33)$$

where the induced potential $V_{\text{ind.},\mathbf{k}}$ is given by

$$V_{\text{ind.},\mathbf{k}} = -\tilde{V} / (1 + \xi^2 (4 - 2 \cos k_x - 2 \cos k_y)), \quad (34)$$

with $\tilde{V}$ given by $\tilde{V} = U_{bf}^2 / U_{bb}$, and ξ is the healing length of the BEC and is given by $\xi = \sqrt{t_b / 2n_b U_{bb}}$. This approach is only valid when $v_b \gg v_f$, so that the fermion-fermion interaction mediated by the bosons can be considered as instantaneous. Away from this limit, retardation effects are present. In this case, one has to consider the frequency dependence of the interaction explicitly (Klironomos and Tsai 2007; Tsai et al. 2005a, b). The full effective interaction, including retardation, is given by

$$V_{\text{ind.}}(\omega, \mathbf{k}) = - \left[\frac{\tilde{V}}{1 + \xi^2 (4 - 2 \cos k_x - 2 \cos k_y)} \right] \frac{\omega_{\mathbf{k}}^2}{\omega^2 + \omega_{\mathbf{k}}^2}, \quad (35)$$

and the static limit (34) is recovered when $\omega_{\mathbf{k}} \gg \omega$. Equation 33 describes the scattering of two fermions from momenta $\mathbf{k}_1$ and $\mathbf{k}_2$ that are

scattered into momenta $\mathbf{k}_3$ and $\mathbf{k}_4$. Momentum conservation at the interaction vertex requires that $\mathbf{k}_4 = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$, and hence, the interaction vertex, $U(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$, depends on three momenta. Its bare value from Eq. 33 can be written as

$$U(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = U_{\text{ff}} + V_{\text{ind.}, \mathbf{k}_1 - \mathbf{k}_3}. \quad (36)$$

For the case with retardation, there is dependence on both the momenta and frequencies of the electrons, so we have $U(k_1, k_2, k_3)$, with $k_4 = k_1 + k_2 - k_3$, where $k_i = (\omega, \mathbf{k})$.

Starting from non-interacting fermions, we ask the general question of what new many-body phases can emerge when the system is subjected to a given interaction $U(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$. Our approach to address this question is the renormalization-group method, described in the next section.

Renormalization Group Method

Starting with a microscopic model of interacting electrons on a lattice, the renormalization-group (RG) method provides the effective model at a given temperature or energy scale (Shankar 1994). The RG is implemented by systematically tracing out high-energy degrees of freedom in a region between Λ and $\Lambda + d\Lambda$, where Λ is the energy cutoff of the problem. In this process, the vertex U is renormalized. At the initial value of the cutoff $\Lambda = \Lambda_0$, the value of U is given by its bare value. For the BFM system we describe here, it is given by Eq. 36. At one loop, the RG flow is obtained from a series of coupled integral-differential equations (Zanchi and Schulz 2000) for all the different interaction vertices $U(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$. The RG equations read as follows:

$$\begin{aligned} \partial_\ell U_\ell(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = & - \int_{p, \omega} \partial_\ell [G_{p\ell} G_{k\ell}] U_\ell(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}) U_\ell(\mathbf{p}, \mathbf{k}, \mathbf{k}_3) \\ & - \int_{p, \omega} \partial_\ell [G_{p\ell} G_{q_1\ell}] U_\ell(\mathbf{p}, \mathbf{k}_2, \mathbf{q}_1) U_\ell(\mathbf{k}_1, \mathbf{q}_1, \mathbf{k}_3) - \int_{p, \omega} \partial_\ell [G_{p\ell} G_{q_2\ell}] \\ & \times \{ -2U_\ell(\mathbf{k}_1, \mathbf{p}, \mathbf{q}_2) U_\ell(\mathbf{q}_2, \mathbf{k}_2, \mathbf{k}_3) + U_\ell(\mathbf{p}, \mathbf{k}_1, \mathbf{q}_2) U_\ell(\mathbf{q}_2, \mathbf{k}_2, \mathbf{k}_3) \\ & + U_\ell(\mathbf{k}_1, \mathbf{p}, \mathbf{q}_2) U_\ell(\mathbf{k}_2, \mathbf{q}_2, \mathbf{k}_3) \} \end{aligned} \quad (37)$$

where $\ell = \ln(\Lambda_0/\Lambda)$, $\mathbf{k} = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{p}$, $\mathbf{q}_1 = \mathbf{p} + \mathbf{k}_2 - \mathbf{k}_3$, $\mathbf{q}_2 = \mathbf{p} + \mathbf{k}_1 - \mathbf{k}_3$, and $G_{k\ell} = \Theta(|\xi_{\mathbf{k}}| - \Lambda)/(i\omega - \xi_{\mathbf{k}})$ with $\xi_{\mathbf{k}} = \epsilon_{\mathbf{f}, \mathbf{k}} - \mu_{\mathbf{f}}$ and $k = (\omega, \mathbf{k})$.

From the general interaction vertices $U(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$, the specific interaction channels, such as charge-density wave (CDW), antiferromagnetic (AF), and superconducting (BCS), can be obtained:

$$V^{\text{CDW}} = 4U_c(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_1 + \mathbf{Q}), \quad (38)$$

$$V^{\text{AF}} = 4U_\sigma(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_1 + \mathbf{Q}), \quad (39)$$

$$V^{\text{BCS}} = U(\mathbf{k}_1, -\mathbf{k}_1, \mathbf{k}_2), \quad (40)$$

where we have used the notation $U_c = (2 - \hat{X})U/4$, $U_\sigma = -\hat{X}U/4$ with $\hat{X}U(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = U(\mathbf{k}_2, \mathbf{k}_1, \mathbf{k}_3)$, and $\mathbf{Q}$ is the nesting vector, $\mathbf{Q} = (\pi, \pi)$.

In a numerical implementation, one discretizes the Fermi surface into M patches, and hence, each of the interaction channels (Eqs. 38, 39, and 40) is represented by an $M \times M$ matrix. At each RG step, we diagonalize each of these matrices. The channel with the largest eigenvalue (with the caveat that a BCS channel needs to be attractive to drive a transition) corresponds to the dominant order. The elements of the eigenvector are labeled by the discrete patch indices around the Fermi surface, and the symmetry of the order parameter is given by this angular dependence.

The RG method for interacting fermions has been extended to also include retardation effects, as for the case of interacting electrons which are also coupled to phonons in a crystal (Tsai et al. 2005a, b). In this case (i) the interaction vertices

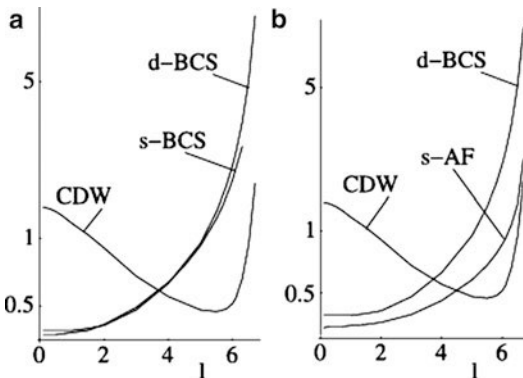
also depend on frequencies of the incoming and outgoing fermions, so the RG equations are written for given external frequencies and the integral over intermediate frequencies cannot be done analytically, and (ii) there are important self-energy corrections (in particular the imaginary part of the self-energy is nonzero). Eliashberg equations for strong-coupling superconductivity has been derived with this method (Tsai et al. 2005a, b) for the case of electrons, with a circular Fermi surface, coupled to phonons. This method has also been applied to other electron-phonon problems (Klironomos and Tsai 2006; Tam et al. 2007) and to mixtures of cold atoms in an optical lattice (Klironomos and Tsai 2007).

Phase Diagram and Subdominant Orders

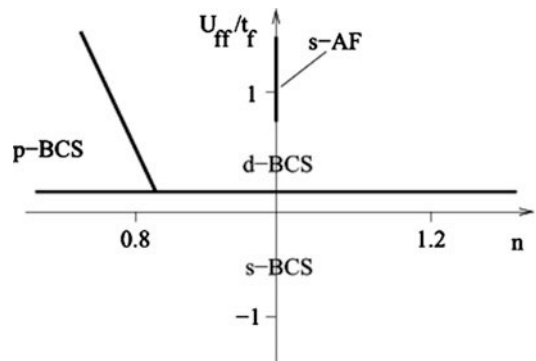
The microscopic parameters in the Hamiltonian Eq. 31 determine the initial conditions for the RG flow and the shape of the Fermi surface. With these, we write the RG flow equations and solve them numerically. We first discuss the case without retardation. For some parameters, we encounter a divergence in the RG flow, indicating the onset of ordering with a gap that is in the detectable regime, i.e., larger than $10^{-3}t_f$. In other regimes, where such a divergence is not reached, one can read off the dominant tendency of the RG flow. In Fig. 9 we show examples of RG flows as a function of ℓ . In Fig. 9a, we show the competition between d -wave and s -wave pairing, with d -wave

being dominant and s -wave being subdominant. In Fig. 9b we show an example with dominant d -wave channel and subdominant AF channel. In both cases we find that for short distances (or high energies) CDW fluctuations are dominant, giving rise to a state that resembles the findings for high- T_c superconductors (Hanaguri et al. 2004; Hoffman et al. 2002; Vershinin et al. 2004). In some situations the many-body states are almost degenerate, and small changes in the initial conditions (i.e., changes in the form of the interactions) can be used to select one particular ground state.

With this procedure we determine the phase diagram of the system, which is shown in Fig. 10. We now discuss the general features of the phase diagram. In the absence of any coupling to the bosons, i.e., for $\tilde{V} = 0$, the system shows s -wave pairing for attractive interaction, $U_{ff} < 0$, and no ordering for $U_{ff} > 0$, i.e., Fermi liquid behavior, except for the special case of half-filling where Fermi surface nesting drives the system to AF order for repulsive interactions and to s -wave pairing (degenerate with CDW) for attractive interaction. If we now turn on the interaction to the bosons, this picture is modified in the following way: The boundary of the s -wave regime is moved into the regime of positive U_{ff} , approximately to a value of U_{ff} where the effective interaction at the nesting vector $\mathbf{Q}$ between the fermions, $U_{ff} + V_{ind,\mathbf{Q}}$, is positive, i.e., for



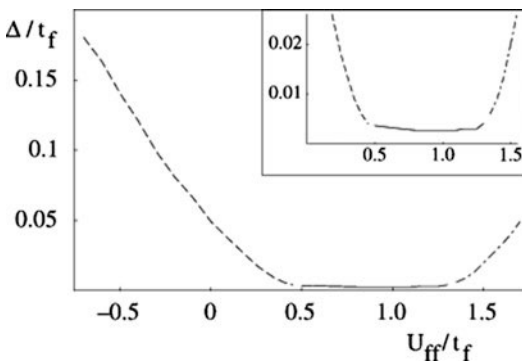
Ultracold Atomic Gases: Novel States of Matter, Fig. 9 RG flow for the different effective interactions (in units of t_f) as a function of the RG parameter l ($\tilde{V}/t_f = 3$ and $\xi = 1$). (a) $U_{ff}/t_f = 0.5$; (b) $U_{ff}/t_f = 1.2$



Ultracold Atomic Gases: Novel States of Matter, Fig. 10 Phase diagram, interaction strength, U_{ff}/t_f , versus number of fermions per site, n , for a Fermi-Bose mixture in a square lattice in 2D ($\tilde{V}/t_f = 2$, $\xi = 1$)

$U_{\text{ff}} \approx \tilde{V}/(1 + 8\xi^2)$. On the repulsive side, and away from half-filling, we find the tendency to form a paired state, either d -wave or p -wave. This tendency becomes weaker the further the system is away from half-filling. We typically find a gap in the vicinity of half-filling, and further away from $\mu = 0$, we find only an increasing strength of the corresponding interaction channel. For the half-filled system, we find that for attractive interactions the degeneracy between s -wave pairing and CDW ordering is lifted, with s -wave pairing being the remaining type of order. For repulsive interactions, we find an intermediate regime of d -wave pairing, and for larger values of U_{ff} , we obtain AF order.

The RG approach also allows the extraction of the many-body gaps in the system through a “poor man’s scaling” analysis of the divergent flow: At the point where the coupling becomes of order of t_{f} , the scaling parameter ℓ reaches the maximum value $\ell_c = \ln(t_{\text{f}}/\Delta)$, where Δ is the value of the gap. Hence, $\Delta/t_{\text{f}} \approx \exp\{-\ell_c\}$ can be obtained from the RG flows such as the ones in Fig. 9. In Fig. 11 we show the gaps of the problem as a function of $U_{\text{ff}}/t_{\text{f}}$ in the half-filled case. One can see that as U_{ff} increases, from negative to positive values, the s -wave gap is replaced by a d -wave gap and finally for an antiferromagnetic gap. As is apparent from this figure, the gap in the d -wave phase is



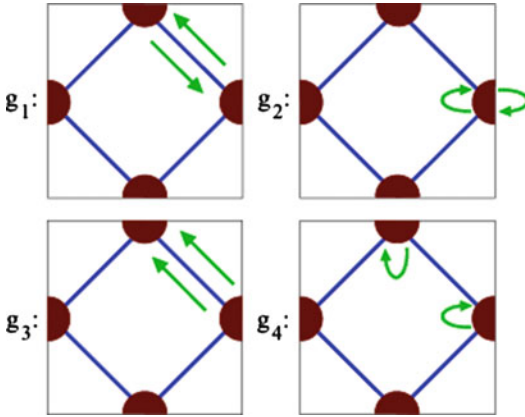
Ultracold Atomic Gases: Novel States of Matter, Fig. 11 Many-body energy gaps at half-filling ($\mu = 0$), as a function of $U_{\text{ff}}/t_{\text{f}}$, for $\tilde{V}/t_{\text{f}} = 3$ and at a fixed value of the coherence length $\xi = 1$. Dashed line, s -wave gap; continuous line, d -wave gap; dotted-dashed line, antiferromagnetic gap. The inset shows a magnified plot of the d -wave regime

much smaller than the gaps of the AF order and the s -wave pairing and, furthermore, almost independent of the value of U_{ff} . The latter is the case because the U_{ff} term is a pure s -wave contribution to the interaction and therefore does not contribute to the d -wave channel. The d -wave channel has an initial contribution which is entirely due to the anisotropy of the induced interaction, which gives only a small value and as a consequence only a small value for the gap. The value of the gap (in units of t_{f}) can be numerically fitted with a BCS expression of the form $a \exp(-b/\tilde{V})$, with the parameters a and b given by $a = 0.31$ and $b = 14.2$.

For a system of spinless fermions, one can simply suppress one of the spin indices in Eqs. 31 and 32. In this case there is a major simplification in the problem since U_{ff} is absent: In a spinless problem there can be only one fermion per site, as per Pauli’s principle. Hence, in the absence of bosons, the spinless gas is non-interacting. The bosons, however, mediate the interaction between the fermions. Since the fermions are in different lattice sites, the pair wavefunction has necessarily a node, and hence, no s -wave pairing is allowed. In other words, in the spinless case the antisymmetry of the wavefunction requires pairing in an odd angular momentum channel. In fact, we find that throughout the entire phase diagram, the fermions develop p -wave pairing. At half-filling we find a similar behavior of CDW fluctuations on short scales, analogous to the flow shown in Fig. 9. One should point out that in real solids the conditions of “spinlessness” behavior is hard to achieve since it usually requires complete polarization of the electron gas, that is, magnetic energies of the order of the Fermi energy (a situation experimentally difficult to achieve in good metals). However, in cold atom lattices this situation can be easily accomplished with the correct choice of atoms.

Finally, when retardation is important, the numerical task of solving the RG flow equations becomes much more demanding. In addition to the discretization of the Fermi surface, one has to also discretize the frequency (for $T = 0$) or

consider a certain number of Matsubara frequencies ($T \neq 0$). This has been done for this Bose-Fermi system only for a fixed density of fermions corresponding to one half (Klironomos and Tsai 2007). In this case the Fermi surface has a diamond shape, and scattering processes are dominated by the van Hove points (corners of the diamond) where the density of states is singular.



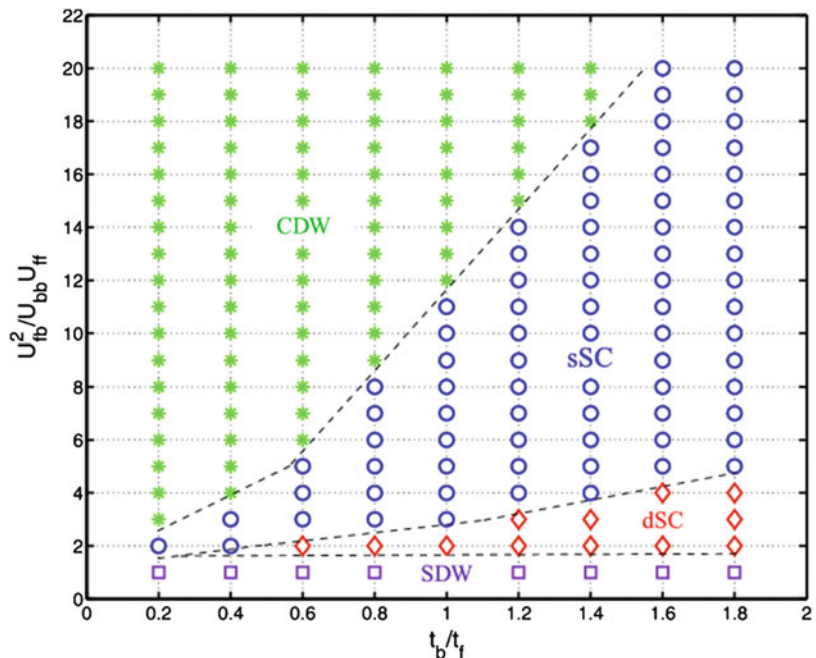
Ultracold Atomic Gases: Novel States of Matter,
Fig. 12 Relevant processes in the two-patch approximation

The Fermi surface can therefore be approximated by the van Hove points only (Schulz 1987) so that the types of relevant processes are reduced, as shown in Fig. 12. Each of the processes still depend on frequencies: $g_i(\omega_1, \omega_2, \omega_3)$, for $i = 1, 2, 3, 4$. The phase diagram is shown in Fig. 13. Retardation leads to additional phases at half-filling and by tuning the lattice parameters, the system undergoes AF (or spin-density-wave SDW), d -wave SC pairing, s -wave-pairing, and CDW. In the limit of $v_b \gg v_f$ discussed previously, when retardation is not important, CDW does not become dominant (Fig. 10). It is at most degenerate with s -wave pairing for $U_{\text{ff}} < 0$. As the bosons become slower, there is stronger tendency for CDW formation (Fig. 13).

Quantum Frustration in Triangular Lattices

It is known that the geometric shape of the lattice is a crucial factor in determining the properties of interacting many-body systems. For instance, localized spins interacting antiferromagnetically on a triangular lattice suffer from the phenomenon of *frustration*, when antiferromagnetic order cannot be achieved because of the particular lattice

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Fig. 13 Phase diagram for $U_{\text{ff}} = 0.4t_f$, $U_{\text{bb}} = 0.8t_f$, and $n_b = 2.5$. Blue circles indicate s -wave SC, red rhombuses d -wave SC, magenta squares AF (also called spin-density-wave SDW), and green stars CDW type of ordering. Dashed lines are guides to the eye



structure. For itinerant fermionic systems, the lattice structure, together with the dispersion relation and the filling fraction, determines the shape of the Fermi surface. The Fermi surface, by its turn, is a crucial factor in determining what type of orders the system can develop. Indeed, for the triangular lattice we consider in this section, which shows a rich and subtle competition between superconducting phases with different symmetries, small changes in the shape of the FS determine which pairing symmetry is dominant. This is a reflection of the “lattice frustration” on the superconducting phases. In solids, this intriguing lattice geometry is realized in materials such as cobaltates (Takada et al. 2003), transition metal dichalcogenides (Withers and Wilson 1986), and κ -(ET)₂X layered organic crystals (J  rome 1991) (if each lattice site is represented by one ET dimer (Kino and Fukuyama 1995)) and has been the subject of several theoretical studies (Baskaran 2003; Choy et al. 2007; Gan et al. 2006; Honerkamp 2003; Lee and Lee 2005; Tsai and Marston 2001; Vojta and Dagotto 1999; Zhou and Wang 2006).

In this section we consider a BFM on a triangular lattice. The geometry of the lattice under consideration here is shown in Fig. 15a. This system is described by a similar Hubbard model as for the square lattice. But now, besides the triangular geometry, we allow for two different values for the hopping amplitudes, for two types of lattice bonds, as indicated in Fig. 15a by dashed and continuous lines. $t_{f,a}$ and $t_{b,a}$ with $a = 1, 2$ are the fermionic and bosonic tunneling amplitudes between neighboring sites, where the index $a = 1$ ($a = 2$) refers to the continuous (dashed) bonds. For the description of the isotropic case, we equate $t_{b/f,1}$ and $t_{b/f,2}$ and define $t_f \equiv t_{f,1} = t_{f,2}$ and $t_b \equiv t_{b,1} = t_{b,2}$. μ_f (μ_b) is the chemical potential for fermions (bosons); U_{bb} , U_{ff} , and U_{bf} are the on-site boson-boson, fermion-fermion, and boson-fermion repulsion energy, respectively.

Just as for the case of a square lattice, we consider the limit of weakly interacting bosons, in which the bosons form a BEC, for which we use the same description. The resulting dispersion relation is now given by

$\omega_{\mathbf{k}} = \sqrt{(\epsilon_{b,\mathbf{k}} - \epsilon_{b,0})(\epsilon_{b,\mathbf{k}} - \epsilon_{b,0} + 2U_{bb}n_b)}$, where the bare lattice dispersion is given by

$$\begin{aligned} \epsilon_{b,\mathbf{k}} = & -t_{b,1}2\cos k_x \\ & -t_{b,2}\left(2\cos\left(k_x/2 + \sqrt{3}k_y/2\right) \right. \\ & \left. + 2\cos\left(k_x/2 - \sqrt{3}k_y/2\right)\right). \end{aligned} \quad (41)$$

For small values of k_x and k_y , $\omega_{\mathbf{k}}$ can be expanded as $\omega_{\mathbf{k}} \sqrt{(2t_{b,1} + t_{b,2})k_x^2 + 3t_{b,2}k_y^2} U_{bb}n_b$, which gives us the two velocities $v_{b,x} = \sqrt{(2t_{b,1} + t_{b,2})U_{bb}n_b}$ and $v_{b,y} = \sqrt{3t_{b,2}U_{bb}n_b}$.

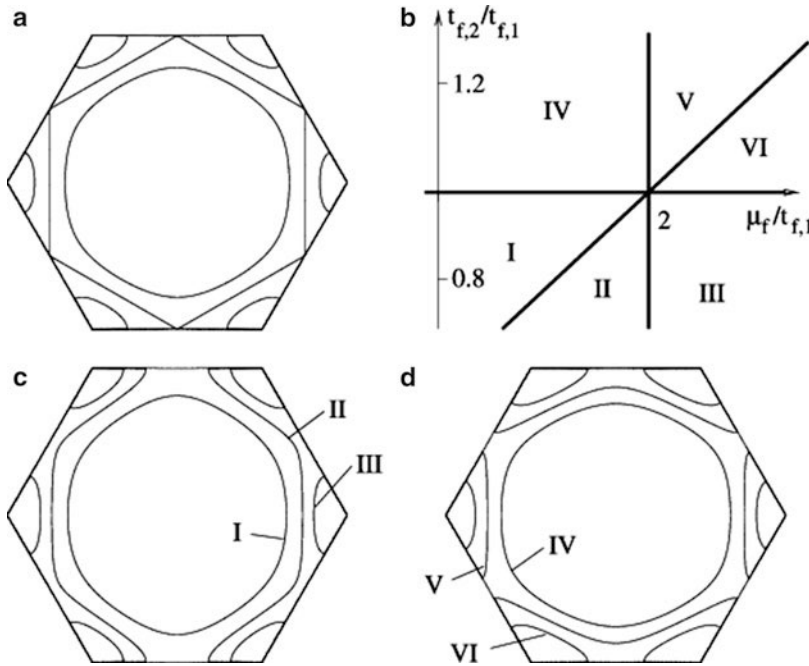
We again assume that these velocities of the condensate fluctuations are much larger than the Fermi velocity, which corresponds to the conditions $v_{b,x/y} > t_{f,1/2}$. Therefore, large bosonic hopping amplitudes, a bosonic density of $\approx 1 - 3$, and some intermediate value for $t_{f,1/2}$ will satisfy this requirement. As before, the bosonic modes can be integrated out, and we obtain an approximately non-retarded fermion-fermion interaction. The induced potential $V_{\text{ind},\mathbf{k}}$ is given by $V_{\text{ind},\mathbf{k}} = -\tilde{V}/(1 + \xi_1^2(2 - 2\cos k_x) + \xi_2^2(4 - 4\cos(k_x/2)\cos(\sqrt{3}k_y/2)))$ with $\tilde{V} = U_{bf}^2/U_{bb}$, and ξ_a are the healing lengths of the Bose-Einstein condensate (BEC) and are given by $\xi_a = \sqrt{t_b/2n_b U_{bb}}$ with $a = 1, 2$. We again arrive at a purely fermionic, non-retarded description of the same form as before. This is the effective model that we study with a numerical implementation of the functional renormalization group. For the isotropic case, perfect nesting occurs at three fourth filling, with three possible nesting vectors, $\mathbf{Q}_1 = (0, 2\pi)$, $\mathbf{Q}_2 = (\pi, \sqrt{3}\pi)$, and $\mathbf{Q}_3 = (-\pi, \sqrt{3}\pi)$, leading to three different possible types of instabilities per density wave channel. For the anisotropic case, only $\mathbf{Q}_1$ can be a nesting vector, for the condition $\mu_f = 2t_{f,1}$. To determine the scale of the gaps, Δ , associated with each of these order parameters, we again use a “poor man’s” scaling estimate, specifically $\Delta \approx \Lambda_0 e^{-\ell_c}$, where ℓ_c is the point at which the RG flow diverges and the instability occurs.

The RG is implemented numerically by discretizing the FS into M patches. For the results shown in this section, $M = 24$ or 36 was used. The CDW, AF, and BCS channels are diagonalized at

each RG step. The dominant instability is the channel that has an eigenvalue (divided by the dimension of the matrix) with the largest magnitude (for BCS one has to ensure that such eigenvalue is negative so that the channel is attractive). Each element of the corresponding eigenvector represents a given FS patch, and hence, the symmetry of the dominant order parameter is reflected on the patch (i.e., angular) dependence of each element around the FS. Using this method, we determine the phase diagram of the system in various limits.

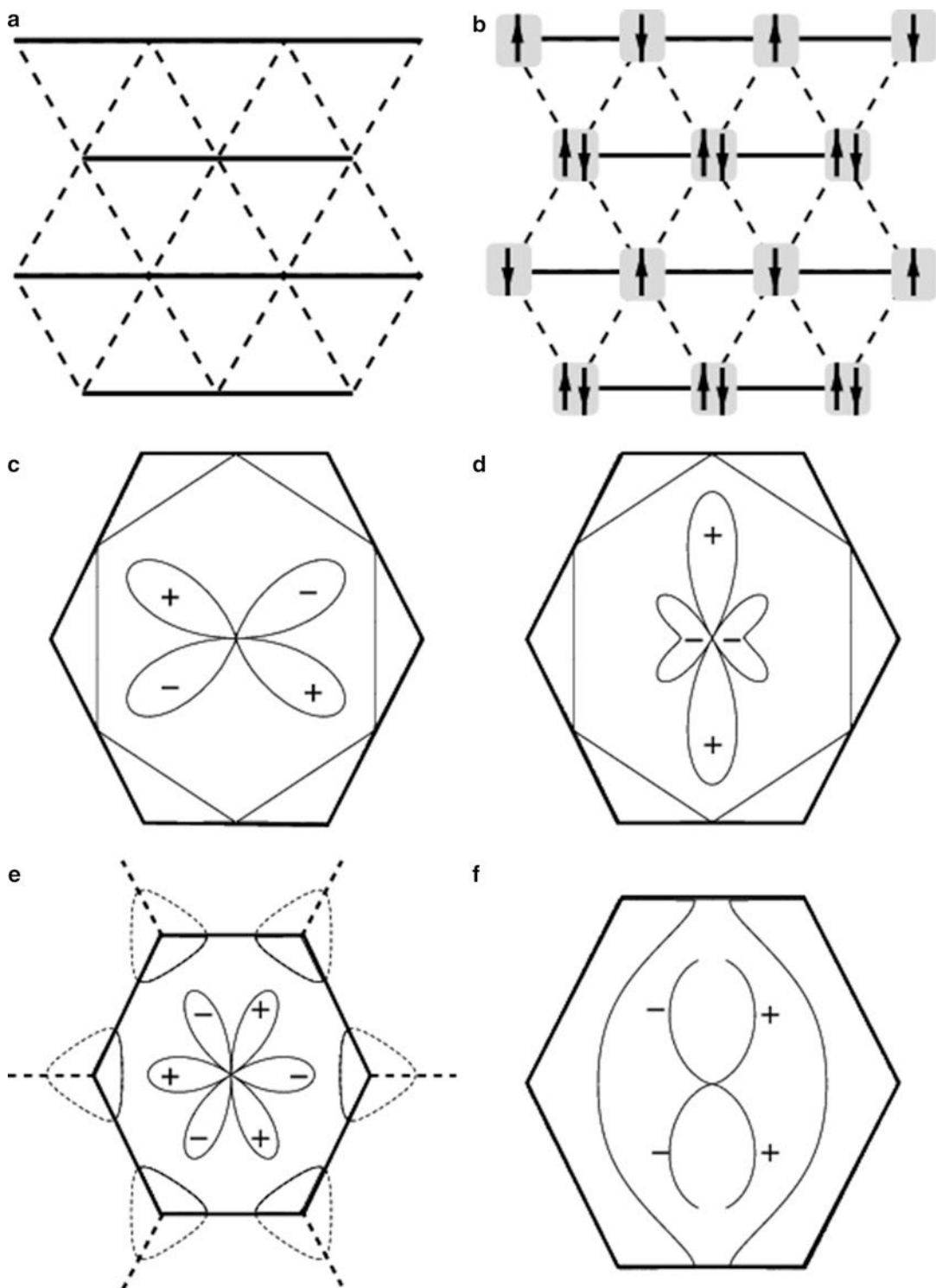
We first consider spin-1/2 fermions on an isotropic triangular lattice, i.e., with $t_{f,1} = t_{f,2} \equiv t_f$. The FS for such a lattice behaves as follows: For small filling the FS consists of one near-circular piece, which then approaches the shape of a hexagon as μ_f approaches the special value $\mu_f = 2t_f$. At this special chemical potential, which corresponds

to three fourth filling, the FS is nested with the three distinct nesting vectors $\mathbf{Q}_i$. For filling fractions larger than three fourth, the FS breaks into six disjoint arcs. Examples for these different regimes are shown in Fig. 14a. Without coupling to the BEC, the fermions form an s -wave pairing phase for attractive interactions, and a Fermi liquid phase for repulsive interactions (ignoring high angular momentum pairing phases predicted by the Kohn-Luttinger theorem (Kohn and Luttinger 1965) which would occur at energy scales much lower than the experimentally accessible regime), except for the specific case $\mu_f = 2t_f$, where the system shows AF order for repulsive interactions. A schematic picture of this order is shown in Fig. 15b for the nesting vector $\mathbf{Q}_1$. This behavior is similar to the one found for isotropic square lattice in the previous section (Mathey et al. 2006): s -wave pairing for attractive interaction



Ultracold Atomic Gases: Novel States of Matter, Fig. 14 (a) Fermi surfaces for an isotropic lattice, for $\mu_f < 2t_{f,1/2}$, $\mu_f = 2t_{f,1/2}$ (hexagonal shape), and $\mu_f > 2t_{f,1/2}$ (six disjoint arcs). (b) Diagram of the different types of Fermi surfaces that can be created on an anisotropic lattice, by varying the ratio $t_{f,2}/t_{f,1}$ and μ_f . (c) Fermi

surfaces for $t_{f,2} < t_{f,1}$, for $\mu_f < 4t_{f,2} - 2t_{f,1}$, $4t_{f,2} - 2t_{f,1} < \mu_f < 2t_{f,1}$, and $\mu_f > 2t_{f,1}$, corresponding to the regimes I–III, respectively. (d) Fermi surfaces for $t_{f,2} > t_{f,1}$, for $\mu_f < 2t_{f,1}$, $2t_{f,1} < \mu_f < 4t_{f,2} - 2t_{f,1}$, and $\mu_f > 4t_{f,2} - 2t_{f,1}$, corresponding to the regimes IV–VI, respectively



Ultracold Atomic Gases: Novel States of Matter,
Fig. 15 (a) Lattice geometry of the system. The

continuous (*dashed*) bonds correspond to the hopping amplitudes $t_{b/f,1(2)}$. For $t_{b/f,1} = t_{b/f,2}$, the lattice is an

and Fermi liquid behavior for repulsive interaction, except at a special filling, for which we find AF order due to nesting. An interesting difference for the triangular lattice is the threefold degeneracy of the AF phase, an indication of frustration.

When the coupling to the BEC is turned on, the isotropic triangular lattice shows a phase diagram of the type shown in Fig. 8. The s -wave pairing phase slightly extends into the regime of positive U_{ff} , because of the induced attractive interaction mediated by the bosonic fluctuations. The regime that showed Fermi liquid behavior in the absence of the induced interaction now shows a rich competition of various types of pairing. In the regime where the density is below half-filling, when the FS is approximately circular, the system shows p -wave pairing. For fillings larger than three fourth, when the FS consists of six disjoint parts, the fermions Cooper pair in a superconducting state with f symmetry. As shown in Fig. 15e, the FS in this regime can also be interpreted as two distinct near-circular Fermi surfaces of holes. In this interpretation each of these two fermionic systems is in an s -wave pairing phase, but the relative phase between the two order parameters is π . At three fourth filling and large values of U_{ff} , the system still shows AF order. However, for smaller values of U_{ff} and also for smaller fillings, two phases with degenerate extended d symmetry develop. These superconducting orders have a sizable g -wave component and are approximately given by

$$\psi_{D_1} = \sin 2\theta + 0.5 \sin 4\theta, \quad (42)$$

$$\psi_{D_2} = \cos 2\theta - 0.5 \cos 4\theta. \quad (43)$$

These order parameters are shown in Fig. 15c, d. The shapes of the order parameters are energetically advantageous because, on the one hand, the order parameter maxima are located at points at

which the system has a high density of states (the “corners” of the FS). Hence, when the superconducting gap opens, there is a large gain of condensation energy coming from these regions on the FS. On the other hand, the d -wave state has lower kinetic energy than the f -wave and hence is selected.

The phase diagram Fig. 8 has a number of similarities to the phase diagram for a BFM on a square lattice, such as the s - and the p -wave pairing phases and the existence of AF order for a nested Fermi surface for large U_{ff} .

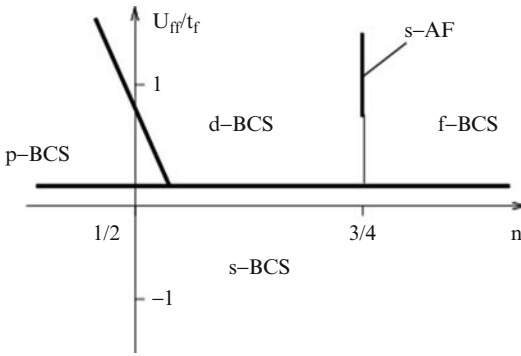
However, the competition of pairing orders for positive U_{ff} and intermediate and large filling is much richer, due to the more complex shape of the Fermi surface.

The energy gaps associated with these order parameters can be determined as we did in the previous section (Mathey et al. 2006), by using a “poor man’s” scaling argument. We find for the s -wave pairing and the AF order that they are around $0.1T_F$, where T_F is the Fermi temperature of the system. For most of the exotic phases, we energy gaps of the order of $0.01 - 0.001T_F$.

We now consider a BFM with spin-1/2 fermions on an anisotropic triangular lattice, i.e., with unequal hopping amplitudes, $t_{\hat{R}(b),1} \neq t_{\hat{R}(b),2}$. The shape of the FS behaves as follows: For $t_{f,2} > t_{f,1}$, as one increases the chemical potential, the FS first breaks into four arcs at $\mu_f = 2t_{f,1}$ and then breaks into six arcs at $\mu_f = 4t_{f,2} - 2t_{f,1}$, corresponding to the regimes IV–VI, in Fig. 14b, d. For $t_{f,2} < t_{f,1}$ the FS first breaks into two arcs at $\mu_f = 4t_{f,2} - 2t_{f,1}$ and then breaks into six arcs at $\mu_f = 2t_{f,1}$ corresponding to the regimes I–III, in Fig. 14b, c. At the special chemical potential $\mu_f = 2t_{f,1}$, the FS is still nested, but there is only one nesting vector along the direction of the bonds with hopping amplitude $t_{f,1}$. In the absence of the coupling to the BEC, the phase diagram has a similar structure as for the isotropic case: s -wave pairing for attractive

Ultracold Atomic Gases: Novel States of Matter, Fig. 15 (continued) isotropic triangular lattice. (b) Schematic representation of the AF order corresponding to nesting vector $\mathbf{Q}_1$. (c, d) Order parameters of the extended d -wave orders D_1 and D_2 . (e) Order parameter of the

f -wave phase. This order can also be interpreted as two s -wave paired hole states whose order parameters are out of phase by π . (f) Order parameter of the extended p -wave phase that appears in anisotropic lattices



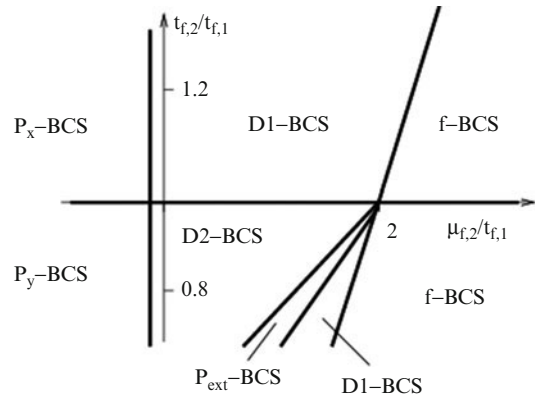
Ultracold Atomic Gases: Novel States of Matter, Fig. 16 Phase diagram of a Bose-Fermi mixture on a 2D isotropic triangular lattice. The vertical axis corresponds to the interaction strength, U_{ff}/t_f , whereas the horizontal axis corresponds to the filling fraction of the fermions per site, n . The other parameters are given by $\tilde{V}/t_f = 3$ and $\xi_a = 1$ with $a = 1, 2$

interaction and Fermi liquid behavior for repulsive interaction, with the exception of the nested FS at $\mu_f = 2t_{f,1}$ where one finds AF order (notice that in this case the filling is not three fourth).

When the coupling to the bosons is turned on, one generates an even more complicated competition of pairing phases for repulsive U_{ff} in the vicinity of the point $\mu_f = 2t_{f,1}$, as is shown in Fig. 17. Generally, for unequal hopping the degeneracy between D_1 and D_2 in Eq. 43 as well as p_x and p_y is lifted: In the regime with $t_{f,2} > t_{f,1}$ ($t_{f,2} < t_{f,1}$), D_1 (D_2) and p_x (p_y) dominate. For $t_{f,2} > t_{f,1}$, in the intermediate regime, in which the FS consists of four disjoint arcs, corresponding to the regime V in Fig. 14, the type of ordering changes from D_1 to f . For $t_{f,2} < t_{f,1}$, the type of pairing also eventually becomes f -wave but first develops two other types of pairing, in regime II in Fig. 14. Firstly, one finds an unusual extended p -wave symmetry, which is schematically shown in Fig. 15f. Its wavefunction is of the form

$$\psi_{P_{\text{ext}}} = \begin{cases} \sin^2 \theta & -\pi/2 < \theta < \pi/2 \\ -\sin^2 \theta & \pi/2 < \theta < 3\pi/2. \end{cases} \quad (44)$$

The second type of pairing that appears before the system develops f -wave pairing is D_1 . These unusual pairing states are energetically favorable



Ultracold Atomic Gases: Novel States of Matter, Fig. 17 Phase diagram of a Bose-Fermi mixture on an anisotropic triangular lattice. The vertical axis corresponds to the ratio $t_{f,2}/t_{f,1}$; the horizontal axis corresponds to the chemical potential μ_f . The other parameters are given by $\tilde{V}/t_f = 3$, $U_{ff}/t_{f,1} = 2$, and $\xi_a = 1$ with $a = 1, 2$

because of the anisotropic shape of the FS. For the regime in which the FS has just barely broken up into two arcs, the order parameter assumes p -wave symmetry and the maxima are located along the y -axis, where the density of states is highest. As the region of open FS widens (see Fig. 15f), this pairing becomes energetically unfavorable, and the system develops D_1 -pairing, so that the maxima of the order parameter can again be located near the point of highest density of states. The energy gaps associated with these order parameters are of the same order of magnitude as for the isotropic lattice.

Finally, we consider a BFM with spinless fermions on an isotropic lattice. Due to the absence of s -wave scattering between fermions of the same spin state, there is no direct interaction, that is, $U_{ff} = 0$. Hence, in the absence of bosons, the spinless gas is non-interacting. The boson fluctuations, however, mediate an induced interaction between the fermions. Due to the antisymmetry of the Cooper pair wavefunction, pairing occurs in an odd angular momentum channel. We find a competition between p - and f -wave pairing symmetries. For small to intermediate filling ($n < 0.65$), p -wave pairing dominates. For larger fillings, for which the FS first approaches the shape of a hexagon and then breaks up into six arcs, the system shows f -wave pairing. Since these larger

fillings of fermions are typically realized in the center of an atomic trap, this result would suggest a comparatively easy way to create an exotic pairing state experimentally. In contrast to this, a spinless BFM on a square lattice only shows p -wave pairing, since for the quadrangular shape of its FS, channels of higher angular momentum are of no advantage energetically.

The many-body states discussed in this section can be observed through various methods: AF order could be revealed in time-of-flight images and Bragg scattering (Stenger et al. 1999), noise correlations (Altman et al. 2004; Fölling et al. 2005; Greiner et al. 2005; Mathey et al. 2008a) can be used to detect the various pairing phases, and laser stirring experiments (Onofrio et al. 1999; Raman et al. 1999) can be used to detect the phase boundary between AF order and pairing. The short-scale CDW fluctuations should give a signature in a photo-association measurement. RF spectroscopy (Chin et al. 2004) can be used to quantify the gaps of the various phases.

Conclusions

In this entry we studied the phase diagrams of various low-dimensional ultracold atom systems. In section “[One-Dimensional Lattices](#),” we studied atomic mixtures in one dimension, using Luttinger liquid theory. We argued that a Bose-Fermi mixture can be naturally looked at as a Luttinger liquid of polarons, and we discussed the rich phase diagrams of commensurate mixtures. In section “[Phase-Locking Transition of Coupled Low-Dimensional Superfluids](#),” we studied the phases of two coupled two-dimensional superfluids at finite temperature. We found that the critical temperature of the phase-locked phase is significantly increased over its bare value, which we propose to use for realizing the Kibble-Zurek mechanism. When interactions between the two superfluids are present, we find additional phases which are partially superfluid and partially disordered. In section “[Bose-Fermi Mixtures in Two-Dimensional Optical Lattices](#),” we used the powerful method of functional renormalization group equations to determine

the phases of Bose-Fermi mixtures in two-dimensional optical lattices. We found an intricate competition of orders, including new types of exotic pairing for triangular lattices. In all these sections, ideas how to probe our predictions were also given.

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Quantum Chaos

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Article Outline

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Glossary

Ergodicity The property of a dynamical system, according to which a single trajectory, starting from almost any initial condition, explores (densely covers) the entire available phase space of physical states.

Integrability A classical Hamiltonian dynamical system of N degrees of freedom is said to be integrable (according to Liouville) if there exist N independent conserved quantities. Integrability implies explicit quasiperiodic solution of the equations of motion.

Periodic orbit theory or trace formula A relationship between certain properties of energy spectrum of a quantized chaotic system and the set of unstable periodic orbits of the corresponding classical chaotic system.

Quantum Loschmidt echo or fidelity A measure of stability of quantum time evolution. It is computed as a Hilbert space inner product of two slightly different quantum time evolutions starting from the same initial state.

Random matrix theory The statistical theory which allows to describe the fluctuation properties of quantum systems in terms of the sets (ensembles) of random Hermitian matrices with appropriate invariant measures.

Wigner surmise Nearest neighbor energy level spacing distribution based on the simplest 2×2 Gaussian Hermitian random matrix models, accurately approximating spacing distributions in complex quantum systems.

Definition of the Subject

As it is now widely recognized, classical dynamical chaos has been one of the major scientific breakthroughs of the past century. Quantum chaos, sometimes called Quantum chaology, studies the manifestations of chaotic motion and related dynamical phenomena in quantum mechanics (Haake 2001; Stöckmann 1999).

More abstractly, one may define as quantum chaos those phenomena of *simple* quantum systems which can be described statistically and exhibit some universal (i.e., system independent) features. By the term *simple* we mean here that the system can be specified by a finite set of parameters or, generally, can be described by a finite amount of information. So we can fundamentally distinguish the phenomena of quantum chaos from similar dynamical phenomena in *disordered* systems – specified in terms of random parameters and which therefore contain infinite amount of information in an appropriate (say thermodynamic) limit.

The universal statistical properties of quantum chaotic systems which have been widely studied include statistics of energy level spectra, statistical and semiclassical structures of the wave functions, and statistical distributions of transition matrix elements (matrix elements of certain physical observables in the energy eigenbasis). These properties are of key importance for understanding quantum state transitions, dissipation,

ionization, and related phenomena. Traditionally quantum chaos has been intimately connected to problems in atomic physics, nuclear physics, mesoscopic solid-state physics, and more recently also to the emerging field of quantum information.

The subject of quantum chaos is at the core of the fundamental and general understanding of the correspondence principle according to which classical mechanics emerges as a limit of quantum mechanics when an “effective” value of the Planck’s constant goes to zero. However, changing perspective and treating quantum mechanics as a fundamental theory and classical mechanics as its convenient approximation, one can ask what happens to the phenomena of quantum chaos in systems which lack the classical limit, such as systems of spin one half or quantum bits (qubits). Still, many of the successful statistical tools developed or widely used in the field of quantum chaos can be applied to understand the dynamical and statistical properties of interacting qubits.

Introduction

Classical Hamiltonian dynamical systems display a rich variety of behaviors (Cornfeld et al. 1982). At one end, we have *strongly chaotic* dynamical systems, which are distinguished by such properties as *algorithmic complexity*, *exponential sensitivity to initial conditions*, *continuous spectrum* and consequent decay of temporal correlations (“loss of memory”), relaxation to equilibrium, and *ergodicity*. Without entering a discussion of the above properties, we notice that rigorous examples of such strongly chaotic systems are billiard balls bouncing inside a table with inward curved boundaries or point mass particles moving freely on any surfaces of constant *negative curvature*.

At the opposite end, there are *completely integrable* or *regular* dynamical systems, which, according to Liouville, are characterized by the existence of as many independent smooth constants of motion as there are degrees of freedom and which are distinguished by analytic predictability of time evolutions and absence of

algorithmic complexity. Consequently, integrable systems have a discrete spectrum of time evolution, do not display relaxation to equilibrium, and due to existence of nontrivial constants of motion, are not ergodic.

Nowadays we know few examples of completely integrable systems, such as an arbitrary system of coupled linear (harmonic) oscillators, the general problem of two moving bodies interacting with a centrally symmetric force, and even many-body models such as the famous Toda lattice which is a system of equal point masses in one dimension interacting with exponentially distance-dependent force. On the other hand we also know that a generic or typical Hamiltonian system is not integrable, neither it is strongly chaotic in a rigorous sense. Instead, we find a variety of intermediate behaviors between completely integrable and strongly chaotic.

A famous Kolmogorov-Arnold-Moser (KAM) theorem states that a small generic (smooth) perturbation of a completely integrable Hamiltonian systems preserves most of the features of regular motion, such as quasiperiodicity or discrete spectrum, for most of initial conditions. However, in the vicinity of the so-called resonant tori (i.e., for initial conditions for which the motion of the unperturbed system has commensurate frequencies), the motion becomes locally (weakly) chaotic even for arbitrary weak perturbations. Still, the relative overall phase space volume occupied by chaotic trajectories decreases to zero faster than any power of the perturbation strength.

However, KAM theory does not describe the only scenario of integrability breaking in Hamiltonian systems. Other types of perturbations, which do not obey the conditions of KAM theorem, are possible which yield physically interesting behavior. One class of such behaviors is the motion in generic polygonal billiards (Casati and Prosen 1999) (namely, billiard tables with the shape of a generic polygon, say a triangle) or the motion of any number of elastically colliding point masses in one dimension. Such systems are neither integrable nor chaotic in the sense of exponential sensitivity or algorithmic complexity.

The fundamental problem of quantum chaos concerns the manifestations in the quantum world

of the various degrees of complexity of classical dynamics, as described by the above hierarchy. Primarily we are interested in *simple*, closed (isolated), and bounded systems for which, as it is known, the spectrum of the Hamilton operator (the generator of the Schrödinger equation) is always discrete. Notice that in classical ergodic theory, discrete spectrum is associated to integrability which is just the opposite of chaos which requires continuous spectrum. In such a situation, quantum mechanics, at most, can follow chaotic classical dynamics only up to the so-called *breaking* time scale t^* after which the quantum motion becomes fundamentally different from the classical one. Precise understanding of this transition phenomena, scaling of the time scale t^* with various physical properties, is at the heart of quantum chaos and shall be briefly discussed in the subsequent sections.

Quantum Chaos: Stationary Aspects

The problems of quantum chaos can be viewed from two different but closely connected viewpoints, namely, the stationary aspects in the energy domain and the dynamical aspects in the time domain. Let us start by discussing the stationary aspects.

It has been recognized as early as in the 1950s by Wigner, and later by Dyson, that many statistical features of energy levels of complex nuclei, or long-lived resonance states, can be adequately described by a simple statistical model of random Hermitian matrices. Wigner's idea was that for a sufficiently complicated quantum system with many degrees of freedom like a heavy nucleus, one assumes that the matrix elements of the Hamiltonian in a *typical* basis can be treated as independent Gaussian random numbers. Such random matrix model has essentially no free parameters and is invariant under almost arbitrary basis changes, and therefore, one can obtain many explicit analytical results.

The simplest and perhaps the main result of random matrix theory (Mehta 1991) predicts that the statistical distribution of spacings between adjacent energy levels, denoted by $S_n = E_{n+1} - E_n$,

properly scaled or normalized such that the average spacing S equals one, obeys universal distributions which only depend on certain symmetry properties. Roughly speaking, they depend on the existence of time-reversal invariance of the Hamiltonian and are, to a high level of accuracy, given by the so-called Wigner surmise:

$$P_\beta(S) = AS^\beta \exp(-BS^2)$$

where the constants A and B are determined from normalization conditions, $\int_0^\infty P_\beta(S) dS = 1$, $\int_0^\infty SP(S) dS = 1$. The integer β is known as universality index and equals $\beta = 1$ for real Gaussian random matrices applying in the time-reversal invariant case and $\beta = 2$ for complex Gaussian random matrices applying in the case where time-reversal invariance is broken. Note that β has also an interesting interpretation as a *level repulsion parameter* since $\beta > 0$ implies repulsive correlations between adjacent energy levels.

Of course, random matrix theory would only remain an interesting mathematical model if it would not have been so immensely successful in describing spectral correlations of complex quantum systems. As already mentioned it started with nuclear spectra for which one is ready to believe that due to immense complexity of interactions, random matrix description is intuitively adequate. However, in the beginning of the 1980s, numerical evidence started to accumulate (Casati et al. 1980; Bohigas et al. 1984) that even the spectra of very simple, but yet nonintegrable and classically chaotic systems exhibit universal level fluctuations described by random matrix theory.

This observation, namely, *that short-range spectral correlations of quantum systems which are strongly chaotic in the classical limit obey universal fluctuation laws which are given by ensembles of random matrices without free parameters*, has been known as *quantum chaos conjecture* and, despite of still not being rigorously proven, remains one of the defining and most important results in the field.

One of the standard paradigmatic models where quantum chaos conjecture has been most often and convincingly demonstrated is quantum

billiards. The stationary Schrödinger problem for a billiard of a point particle of mass m moving freely inside a planar domain (billiard table) $\mathcal{D}$ and colliding elastically off its boundary is simply the well-known Helmholtz (amplitude) equation for the particle wave function:

$$\nabla^2 \Psi(x, y) + k^2 \Psi(x, y) = 0$$

with Dirichlet boundary condition $\Psi|_{\partial\mathcal{D}} = 0$, having a discrete set of solutions $\{k_n, \Psi_n; n = 1, 2, \dots\}$ with a dispersion relation to the eigenenergies $E_n = \hbar^2 k_n^2 / (2m)$. In Fig. 1 we show two examples of a typical integrable billiard (circular billiard) and a typical fully chaotic and ergodic billiard (cardioid billiard proposed by Robnik (Robnik 1983)) – plotting typical trajectories for each and a sequence of few typical chaotic and regular eigenstates.

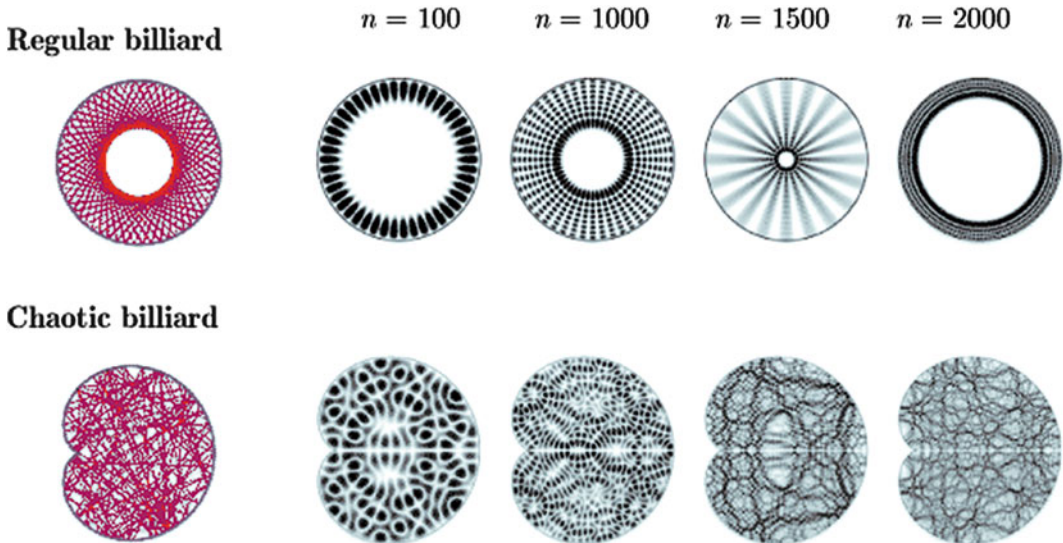
Solving the Dirichlet-Helmholtz problem for a finite domain is one of the most standard problems in linear wave physics and emerges in equivalent forms in gas acoustics, flat electromagnetic (microwave) resonators, transverse waves in optical fibers, etc., the only difference from the stationary quantum problem being the dispersion relation

which connects the frequency of stationary waves to the eigenvalues of the wavenumber k_n .

In Fig. 2 one can observe that spectra of chaotic quantum billiard, hydrogen atom in strong magnetic field, excitation spectrum of NO_2 molecule, microwave electromagnetic spectrum of a three-dimensional chaotic cavity, and even spectra of vibrating elastic solids all exhibit spectral correlations which are given by a Gaussian ensemble of real random matrices.

The universality of quantum statistics of classically chaotic systems applies also to other properties, such as the distribution of a chaotic wavefunction amplitudes, which is Gaussian and very well modeled by the so-called random plane wave superposition (Berry 1977); the distribution of matrix elements of typical observables in the eigenbasis of chaotic Hamiltonians (Feingold and Peres 1986), which is again Gaussian; or even distribution of chaotic Wigner functions (quantum analogues of phase space densities) which is found again to be Gaussian (Horvat and Prosen 2003).

An interesting related mathematical question is the problem of *quantum ergodicity*. For a generic physical observable A , the question is whether its

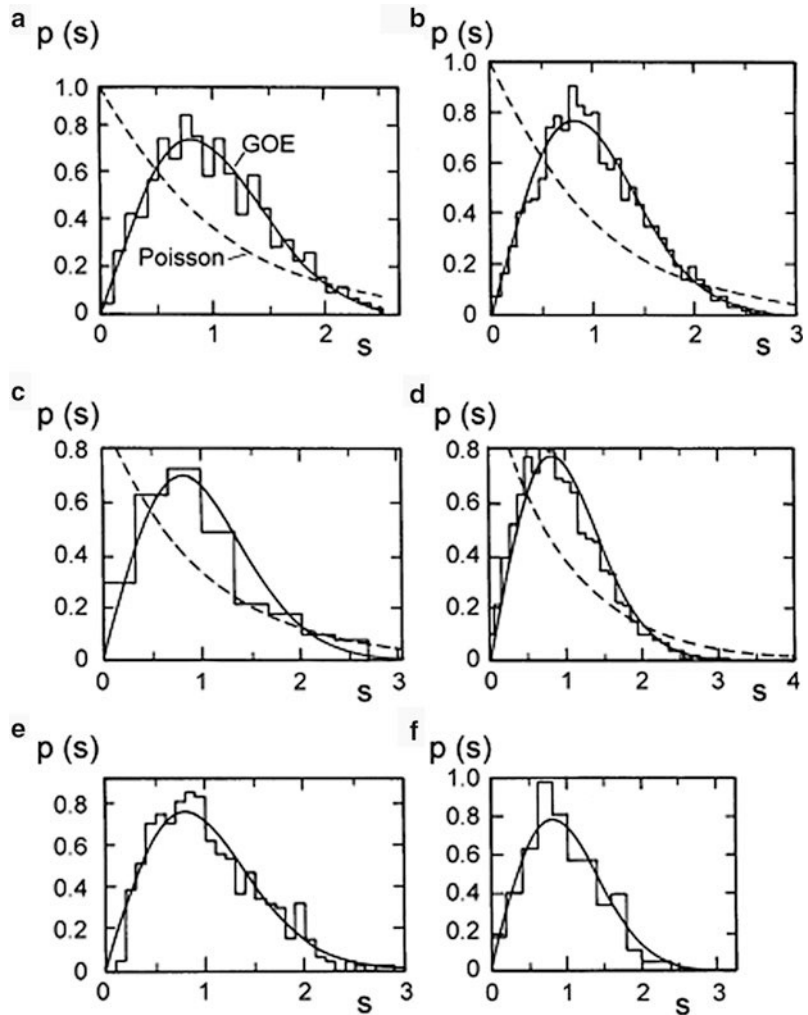


Quantum Chaos, Fig. 1 Typical examples of a regular billiard (circular billiard, *above*) and a fully chaotic billiard (cardioid billiard, *below*). In the *left* side of the figure, we show two typical trajectories in the billiard table, whereas

to the *right*, we depict few examples of wave functions of eigenstates at different sequential level numbers n (Courtesy of Bäcker 2007)

Quantum Chaos,

Fig. 2 Level spacing distributions for (a) the fully chaotic Sinai billiard (Bohigas et al. 1984), (b) a hydrogen atom in a strong magnetic field, (c) an NO₂ molecule, (d) a vibrating quartz block shaped like a three-dimensional Sinai billiard, (e) the microwave spectrum of a three-dimensional chaotic cavity, (f) a vibrating elastic disc-shaped like a quarter stadium (Courtesy of Stöckmann 1999)



expectation value in a given eigenstate approaches, with increasing quantum level number, the microcanonical average of the corresponding classical observable evaluated at the corresponding energy, namely, whether the sequence

$$\{ \langle \Psi_n | A | \Psi_n \rangle - A_{\text{classical}}(E_n); n = 1, 2, 3, \dots \}$$

converges to zero? Mathematicians often relax the above condition to hold for a *subsequence of density 1* meaning that the above property holds for a typical eigenstate, whereas the sequence of exceptions (with semiclassically vanishing statistical weight) corresponds to the famous *scar states* discovered by Heller (1984). For quantum

billiards, the statement of quantum ergodicity is equivalent to the statement of uniform equidistribution of probability density for eigenstates (see e.g., lower panels of Fig. 1). It has been proven (the proof has been announced by Shnirelman (1974) and later worked out by Zelditch (1987) and Colin de Verri  re (1985)) that strongly chaotic billiards, and some other rigorous examples of strongly chaotic systems, are quantum ergodic. However, the minimal classical ergodic properties (like ergodicity, weak mixing, etc.) sufficient for quantum ergodicity are still under debate.

One can now ask similar questions for the other extreme of ergodic hierarchy, namely, for classically regular systems: Are there some universal

features of spectral fluctuations of quantum systems whose classical limit is completely regular? The answer is only partly affirmative, in the sense of an argument which has been originally given by Berry and Tabor (1977a). The starting point of this argument is that the eigenenergies of a completely integrable system with d degrees of freedom can be labeled by a d -tuple of quantum numbers – integers n_j – namely, $E_{n_1 n_2 \dots n_d}$. Berry and Tabor argued that level subsequences, where $d - 1$ quantum numbers are fixed and only one of them is being varied, are *mutually independent*. As the overall spectrum of an integrable system is a superposition of many such almost uncorrelated level sequences, one concludes that any short-range level correlations should be absent. For example, the level spacing distribution for an integrable system should be the same as for a Poissonian distribution of uncorrelated events, namely,

$$P_{\text{int}}(S) = \exp(-S).$$

One has to note that for integrable systems, one should not really expect a universality in the same sense as for chaotic systems. Berry and Tabor's argument cannot in general be turned into a rigorous proof, and for any particular integrable system, one can in principle always find statistical measures which deviate from Poissonian predictions (Casati and Chirikov 1985). For example, a one-dimensional harmonic oscillator has an equidistant (the so-called picket fence) spectrum so its level spacing distribution can be written in terms of a Dirac's delta distribution $P_{\text{harm.osc.}} = \delta(S - 1)$. In other words, as quantum statistical properties are concerned, there is no such thing as *a typical integrable system*. This can be viewed as another manifestation of quantum non-ergodicity of integrable systems.

Even if spectral fluctuations of integrable systems are relatively universal – in the sense as explained above – this is not at all true for other statistical properties of quantized integrable systems, such as wave-function *amplitudes*, sizes, and numbers of *nodal domains* of wave functions, *matrix elements* of typical physical observables, etc. There we find system-specific features which

can hardly be described by some general statistical rules.

The general case of typical quantum systems, say those which can be understood as quantizations of systems with classically mixed phase space with coexisting regular and chaotic orbits, is the most difficult to describe. It is fair to say that quantum chaos of generic systems is still in its infancy. Among the few results which can be mentioned is the semiclassical theory of Berry and Robnik (1984) describing level fluctuations of mixed systems as statistical superposition of independent level subsequences corresponding to each invariant classical phase space component: level subsequences corresponding to areas of chaotic motion are modeled by an appropriate ensemble of random matrices with the relative level density which is given by the classical volume of the chaotic component, and a (single) subsequence corresponding to all regular trajectories is modeled by a Poissonian level sequence of the corresponding overall level density. However, in realistic quantum systems, *tunneling* between chaotic and regular states has to be taken into account, and in spite of few attempts, we are still lacking a general statistical theory of tunneling amplitudes in mixed phase space systems.

It should be noted that statistical properties of energy level fluctuations can be related to classical recurrent phase space structures such as periodic orbits. In particular, for chaotic dynamical systems, one finds a beautiful relationship between semiclassical approximation to the energy spectrum and isolated unstable classical periodic orbits, which is known as Gutzwiller's *trace formula* (Gutzwiller 1991), and is based on stationary phase approximation to Feynman path integral representation of Green's function of the Schrödinger equation. A similar trace formula has been proposed by Berry and Tabor also for classically regular systems (Berry and Tabor 1977b). Related periodic or closed orbit theories have been later developed for describing semiclassical properties of other quantities, for example, scars in chaotic wave functions (Bogomolny 1988; Berry 1989). The trace formula has been believed to be the theoretical tool to attack the proof of quantum chaos conjecture.

Considerable recent progress has been achieved by Müller et al. (2004), building upon an idea of Sieber (2002), who have shown that the correct resummation of a trace formula indeed yields short time expansion of the universal *spectral form factor* (Fourier transformation of the two-point spectral correlation function) which is identical to the one obtained from random matrix theory.

Quantum Chaos: Dynamical Aspects

Classical chaos is a property of time evolution and, as we have seen, requires continuous spectrum of the motion. However, the spectrum of bounded closed quantum systems is always discrete; therefore, genuine quantum chaos which would be a property of asymptotic time evolution is not possible, namely, there is an ultimate breaking time scale t^* which is determined by the density of states $\rho = dE_n/dn$. Indeed, writing a completely general solution of the time-dependent Schrödinger equation as

$$\Psi(t) = \sum_n c_n \exp(-iE_n t/\hbar) \Psi_n$$

one sees that the quasiperiodic nature of time evolution shows up, on average, when the difference of two adjacent phases grows to 2π , namely,

$$t^* = 2\pi\hbar\rho$$

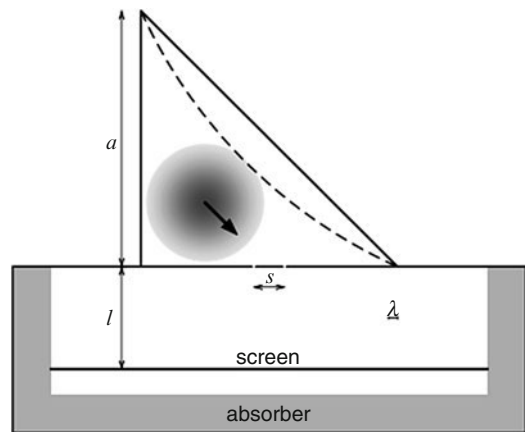
This breaking time scale is also sometimes referred to as Heisenberg time, and after t^* the time evolution in quantum mechanics is dominated by quantum fluctuations.

Thus, genuine quantum chaos is possible only within a time scale $t < t^*$, where quantum phenomena with semiclassical description are possible, such as relaxation, exponential sensitivity, etc. However, not all chaotic phenomena can be observed in quantum dynamics up to t^* ; some are much more short lived. For example, exponential sensitivity to initial conditions can be mimicked by quantum motion only up to the so-called Ehrenfest time

$$t_E = \frac{\ln(A_0/\hbar)}{\lambda}$$

where A_0 is the phase space volume explored by a classical chaotic trajectory, and λ is the classical Lyapunov exponent measuring the exponential rate of divergence $\delta x(t) \sim \exp(\lambda t) \delta x(0)$ of nearby trajectories in classical dynamics. Up to time t_E , Gaussian wave packets centered on classical trajectories can be used for semiclassical description of quantum motion (Heller 1991). Ehrenfest time t_E and Heisenberg time t^* are two essential time scales of quantum chaos.

A simple but fundamental manifestation of quantum chaos is the destruction of quantum interferences by quantum dephasing as a result of chaotic classical dynamics. To illustrate this, let us consider a time-dependent double-slit experiment, where the source is closed inside a two-dimensional wave resonator in the shape of a chaotic billiard (Casati and Prosen 2005). The setting is depicted in Fig. 3. We take an initial Gaussian wave packet with average energy corresponding to about the 1600th excited state of the closed billiard and direct it towards two narrow openings – slits – which are a few (about three) De Broglie wavelengths apart. The wave packet is taken to be as sharply as possible localized in momentum space, so that due to



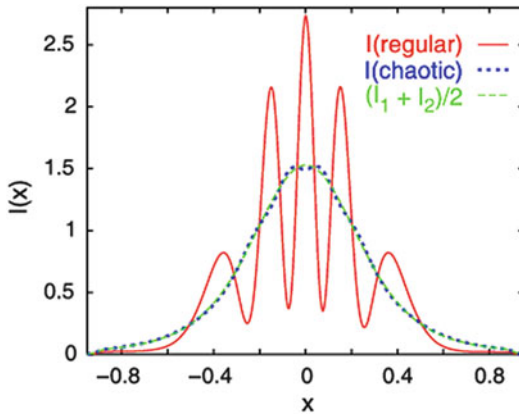
Quantum Chaos, Fig. 3 The geometry of the numerical double-slit experiment. All scales are in proper proportions. The two slits are placed at a distance s on the lower side of the billiard

Heisenberg uncertainty principle, its spreading in position space is of the order of the diameter of the billiard. Then we solve the time-dependent Schrödinger equation and observe the radiation which is transmitted through the two slits to an infinite plane below. We then record the time-integrated probability current density $I(x)$ as a function of the horizontal position x on the screen.

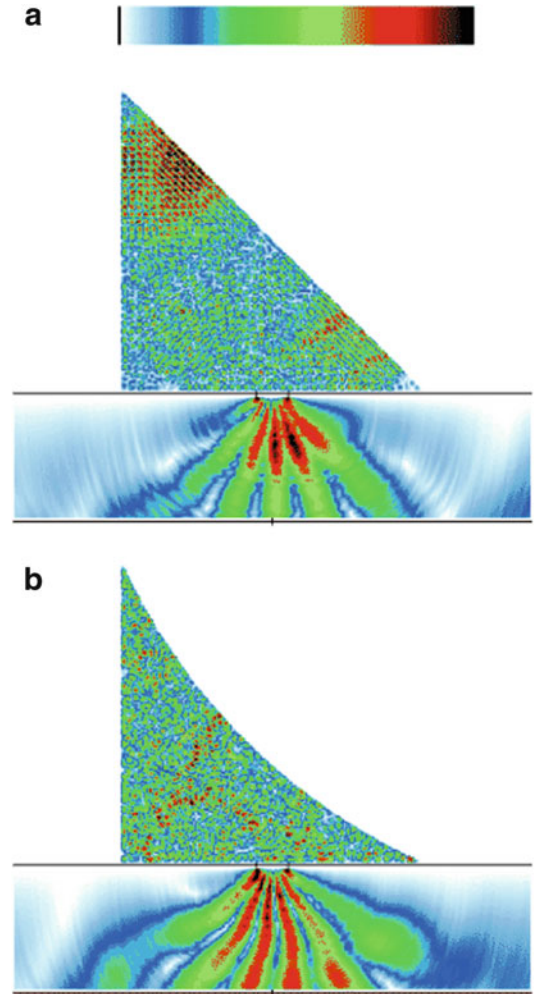
The results of such numerical experiment are shown in Fig. 4. We observe almost no sign of quantum interference if the shape of the resonator is chaotic. This is a manifestation of chaotic dynamics of classical rays and consequently phase randomization of multiply reflected waves impacting onto the slits. For comparison we show an analogous result for a regular geometry of the resonator which is represented by an integrable billiard. Here we find the well-known interference fringes whose location and visibility is a well-controlled function of the initial conditions of the wave packet. In Fig. 5 we show instant snapshots of the probability density at around half the Heisenberg time for chaotic and regular geometry. The crucial difference is that the jets of probability coming out from the two slits have time-

dependent direction in the chaotic case, whereas these directions are frozen in time for the regular geometry.

We note that such a simple numerical experiment has a well-defined analogue (and explanation) in the stationary quantum chaos. Namely, the



Quantum Chaos, Fig. 4 The total intensity after the double-slit experiment as a function of the position on the screen. $I(x)$ is obtained as the perpendicular component of the probability current, integrated in time. The *red full curve* indicates the case of regular billiard, while the *blue dotted curve* indicates the case of chaotic one. The *green dashed curve* indicates the averaged intensity over two 1-slit experiments (where one of the slits is closed), with either the regular or chaotic billiard (with results being practically the same)



Quantum Chaos, Fig. 5 Typical snapshots of the wave function (plotted is the probability density) for the two cases: (a) for the regular billiard at $t = 0.325$ and (b) for the chaotic billiard at $t = 0.275$ (both cases correspond to about half the Heisenberg time). The probability density is normalized separately in both parts of each plot, namely, the probability density, in absolute units, in the radiating region is typically less than 1 % of the probability density in the billiard domain. The screen, its center, and the positions of the slits are indicated with *thin black lines*. Please note that the color code on the top of the figure is proportional to the square root of probability density

intensity $I(x)$, in the far field and narrow slit approximations, can be expressed in terms of spatial autocorrelation of the eigenfunctions of the billiard at the two positions of the slit. It is known (Berry 1977) that chaotic eigenfunctions are characterized by decaying spatial correlations – hence the destruction of interference pattern – whereas eigenfunctions of regular systems have long-range spatial correlations.

Another important aspect of time-dependent quantum chaos is the study of the so-called Loschmidt echoes or fidelity decay (Gorin et al. 2006). This quantity has been proposed by Peres (1984) as a natural analogy in quantum mechanics of Lyapunov exponents and sensitive dependence to initial conditions. Let $U_0(t)$ represent some unitary quantum mechanical evolution operator, e.g., $U_0(t) = \exp(-iHt/\hbar)$ where H is the Hamiltonian, and let $U_\varepsilon(t)$ represent a perturbed evolution, where ε is some small perturbation strength parameter. Quantum Loschmidt echo is defined in terms of fidelity (square modulus of Hilbert space inner product) of a state of perturbed time evolution $|\Psi_\varepsilon(t)\rangle = U_\varepsilon(t)|\Psi(0)\rangle$ with respect to time-evolved state of the unperturbed evolution $|\Psi_0(t)\rangle = U_0(t)|\Psi(0)\rangle$, namely,

$$F(t) = |\langle\Psi_0(t)|\Psi(t)\rangle|^2 \\ = |\langle\Psi(0)|U_0(t)U(t)|\Psi(0)\rangle|^2$$

The first expression (fidelity) can be interpreted as the probability that two nearby quantum evolutions end up in the same state, whereas the second expression (Loschmidt echo) is the probability that the state after forward perturbed time evolution composed with time-reversal operation and (backward) unperturbed evolution for the same amount of time end up in the same (initial) state. The equivalence of the two expressions is a simple consequence of the unitarity of quantum dynamics. The fidelity is a measure of stability of quantum motion. Note that the formalism of Loschmidt echoes can be closely connected to the theory of decoherence in open quantum systems (Gorin et al. 2006). For example, in many interesting specific situations, the Loschmidt echo can be used to bound or estimate certain standard measures of decoherence.

For a semiclassical understanding of Loschmidt echoes, it is very useful to write the expression of quantum fidelity in terms of the Wigner phase space function

$$W_\varepsilon(q, p, t) = (2\pi\hbar)^{-d} \\ \int d^d r \langle q - r/2 | \Psi_\varepsilon(t) \rangle \langle \Psi_\varepsilon(t) | q + r/2 \rangle \exp(ip \cdot r/\hbar)$$

corresponding to state $|\Psi_\varepsilon(t)\rangle$, namely,

$$F(t) = (2\pi\hbar)^{-d} \int d^d q d^d p W_0(q, p, t) W_\varepsilon(q, p, t)$$

It is known that the Wigner function of an initial Gaussian wave packet follows the classical Liouville equation for times below the Ehrenfest time. It can also be easily shown that for short times, the corresponding *classical fidelity* computed in terms of classical phase space densities decays with the same rate with which nearby orbits diverge, namely, with the Lyapunov exponent (Gorin et al. 2006). Therefore, for $t < t_E$, quantum fidelity decays with the perturbation-independent rate given by the classical Lyapunov exponent λ , $F_{\text{lyap}}(t) \sim \exp(-\lambda t)$.

For times between Ehrenfest and Heisenberg time, $t_E < t < t^*$, and correspondingly small perturbation strength so that the fidelity is appreciable, the decay of Loschmidt echo can be computed using time-dependent perturbation theory, or Fermi golden rule, and one obtains $F_{\text{fg}}(t) \sim \exp(-\varepsilon^2 \sigma t)$ where the coefficient σ is equal to average square of near-diagonal matrix elements of the generator of the perturbation. The quantity σ can be semiclassically computed in terms of integrated time-correlation function of the classical perturbation (Gorin et al. 2006).

For even larger times, $t > t^*$, the quantum dynamics is dominated by fluctuations, and fidelity decay, provided ε is small enough, can be computed by static quantum perturbation theory which leads to the Gaussian decay $F_p(t) \sim \exp(-2\varepsilon^2 \sigma t^2/t^*)$.

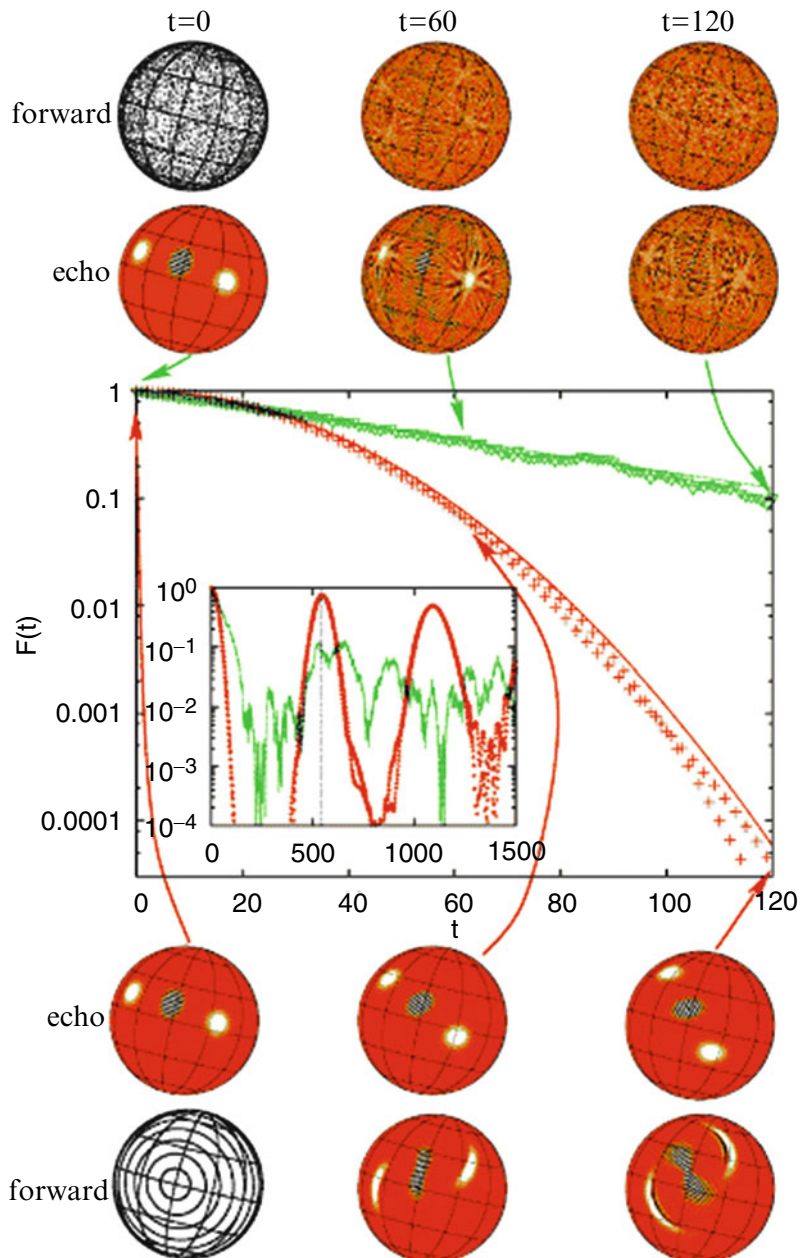
On the other hand, fidelity decay for classically integrable (regular) systems is somewhat simpler but less universal – namely, it depends on the structure of invariant tori of the integrable system

and on the initial state. For initial Gaussian wave packets, the decay of fidelity is typically faster than for chaotic systems, which is a manifestation of *ballistic* nature of regular dynamics as opposed to *diffusive* nature of chaotic dynamics. In Fig. 6, we demonstrate the decay of fidelity for Haake's kicked top model (Haake 2001) and compare the regimes of regular and chaotic dynamics for the

same initial coherent (Gaussian) state and the same value of perturbation parameter. Both cases can be theoretically described and understood (Gorin et al. 2006). For illustration we plot the Wigner functions of the time evolution as well as the Wigner function of the echo dynamics – perturbed forward evolution composed with unperturbed backward evolution. Note that the

Quantum Chaos,

Fig. 6 Fidelity decay for chaotic (*top curve and pictures*) and regular (*bottom curve and pictures*) kicked top. Initial conditions and the perturbation are the same in both cases, and theoretical formulae, with the only input given in terms of classical dynamics, are shown with *full curves* (see Heller 1991 for details). Wigner functions after forward and echo evolution are shown for illustration of the ballistic versus diffusive mechanisms



Wigner function of a quantum top (spin) is defined over a surface of the sphere.

Quantum chaos has been studied also in unbounded systems with infinite classical phase space, such as the kicked rotator (Casati and Chirikov 1995), where classical chaos – through decaying temporal correlations – gives rise to deterministic diffusion. It has been shown (Casati and Chirikov 1995; Casati et al. 1979; Fishman et al. 1982) that the role of classical deterministic chaos in kicked one-dimensional systems with infinite momentum space is analogous and sometimes even formally equivalent to the role of disorder in one-dimensional tight-binding model of a solid. In fact the phenomenon of *dynamical localization* has been discovered (Casati et al. 1979) in full analogy with Anderson localization in disordered one-dimensional solids.

Applications of Quantum Chaos

Theoretical phenomena of quantum chaos have been applied or experimentally observed in a variety of fields. Far from being complete we just mention a few.

Atomic Physics

One of the first successful applications of the ideas of quantum chaos has been a theoretical explanation of multiphoton ionization experiments with hydrogen in microwave field which were performed by Bayfield and Koch (1974). Single hydrogen atoms prepared in very elongated states with high principal quantum number were injected into the microwave cavity and the ionization rate was measured. Even though the microwave frequency was well below the ionization energy, in fact even lower than the transition energy to the next excited energy level, it was found very surprisingly that very efficient ionization occurred when the electric field intensity exceeded a certain threshold value. The theoretical analysis (described, e.g., in Casati and Chirikov 1995) explained the threshold intensities as critical values for the onset of chaotic diffusion in phase space. Quite interestingly, it has been shown that classical mechanics alone accurately

describes the results of experiment, namely, in the situation above the delocalization border (which has been predicted theoretically (Casati et al. 1984)) and in the semiclassical regime of high principal quantum number, where an effective value of the Planck constant is sufficiently small. However, in Casati et al. (1984) it has been shown that dynamical localization can take place in hydrogen atom, and this has been experimentally observed in Bayfield et al. (1989), Galvez et al. (1988).

A second notable experimental achievement has been the observation of dynamical localization, in fact a realization of quantum mechanical kicked rotor in terms of cold Cesium atoms in a standing wave of kicked electric field by the Raizen's group (Klappauf et al. 1999).

Mesoscopic Solid-State Physics

The ideas of quantum chaos have been extensively investigated in mesoscopic solid-state systems, in particular in the studies of quantum transport in the ballistic regime, where the mean free path of the electrons is much larger than the device.

Perhaps it is worth mentioning the discovery of universal conductance fluctuations (Marcus et al. 1992) which correspond to Ericson fluctuations in nuclear physics. It has been shown – by measuring the so-called magnetoresistance in quantum dots (2d conducting structure of a size of the order of a micrometer) – that the conductance fluctuations have some universal statistical features if the shape of the quantum dot represents a chaotic billiard. Universal conductance fluctuations have been later extensively discussed theoretically and explained in terms of random matrix theory (see, e.g., review Beenakker 1997).

Quantum Information

Chaotic quantum dynamics is effective in producing entanglement, which is a key resource for quantum information processing (Nielsen and Chuang 2000; Benenti et al. 2004). This has been demonstrated theoretically with many chaotic toy models; see, e.g., Žnidarič and Prosen (2003). Perhaps it deserves to be mentioned that two of these models, namely, the quantized Baker

map and the quantized sawtooth map, have been realized in a real-world quantum computer (Weinstein et al. 2002). Dynamical chaos can also be explored to engineer robust and accurate decoupling schemes for processing quantum information in the presence of static noise (Gorin et al. 2006).

Wave Chaos

There are many applications of the ideas and mechanisms of quantum chaos outside of quantum mechanics. For example, essentially all the stationary aspects of quantum chaos, and sometimes even some dynamical aspects provided the change in dispersion relations is taken into account, are being beautifully demonstrated in the planar electromagnetic microwave resonators since the early 1990s by the groups of Stöckmann (see, e.g., Stein and Stöckmann 1992), Richter (see, e.g., Richter 2001) and Sridhar (see, e.g., Sridhar 1991). Very impressive “quantum chaos” experimental studies were conducted in acoustics, namely, with blocks of vibrating solids; see, e.g., Ellegaard et al. (2001), Kuhl et al. (2005). It turns out that experimentally feasible quality (Q) factors in elastodynamics resonators can be much larger than in microwave billiards, however, the complication here being that the underlying amplitude wave equation is of fourth order and cannot be interpreted as a Schrödinger equation. Still, using the universality of quantum chaos, one can argue (and find) that statistical properties of resonance frequencies are described by the same statistical random matrix theory (Fyodorov et al. 2005). We may also mention a recent application of quantum chaos to optical fibers (Doya et al. 2001). Another impressive extension of quantum chaos is the nonlinear wave-optics, namely, to engineering of directed stimulated emission of micron-size and chaotic billiard-shaped semiconductor lasers (Harayama et al. 2003).

Future Directions

By now quantum chaos of single – or few particles – systems is relatively well understood. Among open future problems, we should perhaps

mention the case of systems with mixed phase space being neither completely integrable nor fully chaotic. In such systems, one of the most important problems is to derive a quantitative theory of tunneling rates between classically disjoint phase space components.

Most of the results so far obtained in the field of quantum chaos are based on numerical evidence, and we are still lacking of rigorous proofs. For example, we are missing the proof of quantum chaos conjecture, the precise conditions (ergodic properties of the underlying classical system) under which it holds, precise statements about quantum ergodicity in general Hamiltonian systems, etc.

However, one of the key challenges for the future is to understand and apply dynamical chaos mechanisms to quantum systems of many interacting particles. In particular it seems that complete integrability of many-body systems implies anomalous nonequilibrium statistical behaviors, such as ballistic transport, and it seems necessary to operate in the regime of quantum chaos in order to validate diffusive statistical laws in many-body transport. Furthermore, it seems that quantum chaos in many-body systems is intimately connected to the impossibility of efficient simulation of such systems on classical computers. See, e.g., Prosen (2007) for a recent review of these topics.

At the general level, we recall that while in classical mechanics there is a very well-developed ergodic theory which is important for understanding equilibrium and nonequilibrium properties of classical physical systems, in quantum mechanics, there is not, so far, a well-established theory. A theory would be required which could explain the asymptotic relaxation process (in the correct order of limits, namely, letting the time to infinity at last) in the presence of a purely discrete spectrum and in the absence of exponential instability.

We close on a more speculative note. In quantum mechanics, we are always facing with the problem of the measurement device which should be treated as a macroscopic classical system. As for such, classical chaos and exponential instability are present. This is indeed even necessary since by its purpose, a measurement device must be unstable because a microscopic intervention must produce a macroscopic effect. The

importance of chaos in the quantum measurement is that it destroys the coherence of the initial pure state to be measured converting it to an incoherent mixture. In the existing theories of quantum measurement, this is described as the effect of external noise. Chaos theory allows to get rid of this unsatisfactory assumption and to develop a purely dynamical theory of loss of quantum coherence. Still, a fundamental problem remains open, namely, the redistribution of probability according to the result of the measurement: the so-called collapse of the wave function which remains to be understood.

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Networks: Structure and Dynamics

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Article Outline

Glossary
 Definition and Relevance
 Introduction
 Structural Properties of Complex Networks
 Dynamics on Complex Networks
 Future Directions
 Bibliography

Glossary

Simple graph or network A group of N nodes (vertices) among which there exist L undirected connections (links, edges), identical in strength.

Directed graph A group of nodes among which connections are directed.

Weighted network A group of nodes among which connections are not identical in strength, but carry a weight.

Bipartite network A network with more than one type of node, in which connections only exist between different node types (the definition can be relaxed to a network where most, but not all links run between vertices of different types).

Adjacency matrix A An $N \times N$ matrix representing the network, whose elements a_{ij} are equal to 1 when there is a link from node i to j , zero otherwise.

Degree distribution $P(k)$ The probability that a node of a network, chosen uniformly at random, has degree k .

Scale-free network A network in which the tail of the degree distribution follows a power law (strictly speaking, the term scale-free implies $P(k) \sim k^{-\gamma}$, however, it is often used for networks where the tail of the distribution follows a power-law).

Degree exponent γ The power law exponent of the (tail of the) degree distribution.

Scale-free model A growing network model proposed by Barabási and Albert (1999). The model builds a simple graph starting from a small connected group of nodes, to which new nodes are added one by one. These new nodes connect to m old nodes with probabilities that increase linearly with the degree of the old nodes.

Shortest path (geodesic path) The smallest collection of links that form a path through the network from one vertex to another.

Diameter D The length of the largest geodesic path in a network.

Small-world network A network in which the average shortest path length grows logarithmically (or slower) with N .

Node betweenness (betweenness centrality or load) The number of shortest paths between nodes of the network that run through a given node (Freeman 1977).

Edge betweenness The number of shortest paths between nodes of the network that run through a given edge.

Clustering coefficient C The fraction of connections that are realized between the neighbors of a node:

$$C_i = \frac{2 n_i}{k_i(k_i - 1)},$$

where n_i denotes the number of links connecting the k_i neighbors of node i . (The average clustering coefficient is given by $\langle C \rangle = \frac{1}{N} \sum_i C_i$. An alternative global measure of clustering, also called *transitivity*, is the fraction of node triples that are linked into triangles.)

Assortativity coefficient A measure of the tendency of links to run among nodes that are

similar in some respect. If the similarity is described by a scalar quantity (most often the node's degree), then the assortativity coefficient is given by

$$r = \frac{\sum_{x,y} xy(e_{x,y} - a_x b_y)}{\sigma_a \sigma_b},$$

where x (y) is the scalar at the origin (end) of a link, $e_{x,y}$ denotes the fraction of all edges in the network that go from nodes with value x to ones with value y , a_x (b_y) is the fraction of edges that start (end) at a link with values x (y), and σ_a (σ_b) is the standard deviations of the distributions of a_x (b_y) values (Newman 2003).

Modularity Q The number of links between nodes within the same community minus the number expected by chance:

$$Q = \frac{1}{2L} \sum_{i=1}^N \sum_{j=1}^N (A_{ij} - P_{ij}) \delta_{g_i, g_j},$$

where node i (j) belongs to the community g_i (g_j). P_{ij} gives the expected number of links between two nodes if the network is random with respect to communities (Newman and Girvan 2004). In the simplest case, in which the null model is a random network, $P_{ij} = 2L/N^2$. A more suitable assumption is $P_{ij} = k_i k_j / 2L$, which preserves the degree distribution of the network in question (the expected degree of node i is $\sum_j P_{ij} = k_i$) (Newman 2006).

Definition and Relevance

Scientific research has had a long history of bottom-up approaches, which break the system into small or elementary constituents and map out interactions between these components. The Standard Model describing elementary particles and the four types of interactions governing our world is perhaps the most successful example. Biology has developed a very detailed description of cellular components such as the DNA molecule or the various proteins and metabolites. Furthermore, many of the interactions that govern a cells

life have been investigated in great detail, but mainly in isolation: transcription of DNA, protein assembly, enzyme function, etc. Perhaps not surprisingly, the first attempts to understand complexity in physics were focused on small, simple system with complex dynamics: chaos theory. Nonetheless, large natural or social systems, like a cell, an ecosystem or the Internet are much more intuitive examples of complex systems. A meaningful description of these systems requires more than a mere account of the constituent parts: one does not understand the way the Internet works by detailing the physical characteristics of computers. Nor is the sequence of a cell's genome the final tool for understanding its behavior.

Complex systems display characteristics that are fundamentally determined by their organization, emergent phenomena created by all the interacting constituents. In many cases, if one takes a step back, avoiding the details of the interactions, a complex system as a whole is made up of an assemblage of generic elements and connections; in other words, it looks like a network. For example, a cells metabolism is maintained by a biochemical network, whose nodes are substrates and links chemical reactions (Jeong et al. 2000). Equally complex webs describe human societies, whose nodes are individuals and links represent social interactions (Wasserman and Faust 1994), the World Wide Web (WWW) (Albert et al. 1999; Broder et al. 2000), where nodes are Web documents connected by URL links, the scientific literature, whose nodes are publications and links citations (de Solla Price 1965; Redner 1998; Redner 2004), or language, made of words linked by various syntactic or grammatical relationships (Dorogovtsev and Mendes 2001b; Ferrer i Cancho and Solé 2001; Sigman and Cecchi 2002). Due to the diversity and large number of the nodes and interactions, the system-level characteristics of these networks remained largely unknown and unexplored prior to the last decade. At the same time, the inability of contemporary science to address the properties of complex networks limited advances in many disciplines, including molecular biology, computer science, ecology and the social sciences. The recent availability of system-level

data on the network of interactions in large numbers of systems has opened the door for interdisciplinary research in fields where the behavior of the system as a whole is a central question. Recognizing generic organizational principles and order behind diversity and apparent randomness in these different systems has certainly been a surprise along the way.

Introduction

The explosion of available data describing interaction of hundreds to millions of components in systems like the Internet or the protein interaction network is a recent development for the study of complex systems. Nonetheless, networks are not new to mathematics or the social sciences. Graph theory was born from the famous Königsberg bridge problem and its even more famous solution by Euler in 1736 (Euler 1741). The problem was simple: find a closed walk that visits each of Königsberg's seven bridges once, but only once. The trouble was, nobody could find such a walk. Euler drew a four-node graph of the pieces of land connected by the bridges and showed that graphs that have nodes with odd degrees cannot have closed self-avoiding paths. (All four pieces of land in Königsberg are connected via an odd number of bridges). Euler's emphasis on the topology of the bridge problem as key to the solution marks the starting point of two prolific subfields of mathematics: topology and graph theory.

The early 1920's witnessed the birth of social network analysis, a subfield of sociology trying to understand how social interactions organize. Data gathering methods limited the size of the networks studied, nonetheless many network measures important today were defined: degree distribution, betweenness, clustering and the small world effect.

In the 1950's two prolific hungarian mathematicians, Erdős and Rényi, took the challenge of describing the structure of large social networks from social science to mathematics and formulated their famous random graph model (Erdős and Rényi 1959, 1960). Their key innovation

was a statistical approach to graph theory: their theorems were proved on the set of all networks generated by the rules of their model. Their random network rules were simple: take N nodes and connect each pair with probability p . They found that above a certain threshold probability the ensemble of random graphs undergoes a percolation-type phase transition from a graph made of small disjoint subgraphs to one with a giant component comparable with the system size. Random graphs have a Poissonian degree distribution: they are homogeneous networks with a well-defined average degree. Erdős and Rényi pointed out that random networks are "small worlds": their diameter scales with the logarithm of system size (node number), quite different from the power-law relationship that holds for regular lattices.

The Erdős–Rényi model guided our thinking about complex networks until the end of the 1990's, when two seminal papers triggered a very rapid growth of the field which today is called complex networks research. The first paper, published by Watts and Strogatz (1998), showed that natural systems such as the neural network of the *C. Elegans* worm, the power grid and the network of movie actors connected by feature films have a topology somewhere between regular lattices and random graphs. These networks have large clustering coefficients, but also the small world property. The small-world model presented in the paper is the first important step away from the random world of the Erdős–Rényi graph. The second paper, published one year later by Barabási and Albert, showed that the degree distributions of the movie actor network, the WWW and the power grid are not Poissonian: they have a power-law tail, inspiring the term scale-free networks (Barabási and Albert 1999). The list of power-law tailed degree distributions measured on natural and man-made systems is still growing, with degree exponents that rarely fall outside the (2,3) interval. Power law degree distributions tell us that most real networks are highly heterogeneous: the majority of nodes have very small degree, but a few hubs with degrees orders of magnitude larger than the average also exist, along with nodes with degrees of all scales

in between. A good example is the US airport network connected by direct flights: Chicago and Atlanta at the high end of the degree scale, the numerous regional airports at the low end.

Naturally, the sudden explosion of data and tools to explore them brought us closer to the heart of questions fundamental to understanding complex systems: what drives their organization, what defines their emergent properties. What do these networks do, what is their function? This question is natural to biology. A metabolic network has a well-defined job in the living cell: it fuels the cell with energy, nutrients and building blocks, and it does so adaptively and robustly. Man-made complex networks, such as the Internet or WWW, the power grid or the network of synonyms in a language also perform well-defined functions. In contrast with the delicate and well-thought-out internal structure of a computer, these systems were not designed from scratch with their function in mind: they evolved and emerged naturally. Also in contrast with the fragility of a computer (pull out a random element and it stops working), complex systems in biology and technology have a remarkable resilience to random node failure: the internet does not die when a few routers go down, in fact this probably is its normal mode of operation.

Questions about the characteristics mandated by function, common to all these systems, along with questions about the selection principles that shape these structures, are at the heart of our quest to understand complex function. These questions are typically formulated in terms of the dynamics natural to the network in question: metabolic flux driven by enzymes, packet traffic on the internet, web browsing, electric current flow on the power grid, the spread of HIV on the sexual contact network, etc. Understanding how structure affects dynamics and vice versa is in the spotlight of complex networks research today.

Structural Properties of Complex Networks

Let us look at the metabolism of a cell as an example that highlights the increasingly detailed

ways one can pose the question: what is the large-scale structure of cellular metabolism? At first glance, the metabolic network is a *simple graph* in which metabolites (the nodes) are connected by chemical reactions. This representation tells us whether the network is homogeneous in degree or has hubs, whether it is a “small world”, whether it has a community structure. A more detailed description of the system takes into account the direction of chemical reactions, since a large number of them are not reversible in a living cell. This leads to a *directed network* in which the in- and -out-degree distributions can be different and paths are directed. The next step is a *weighted network*: metabolites are characterized by their concentrations in the cell, edges are weighted by fluxes carried by reactions. A different way of adding complexity to the representation is by constructing a *bipartite graph*, where metabolites on one side connect to reactions on the other.

The above example suggests a natural organization for this section: presentation of simple graphs and their characteristics followed by more detailed networks, in parallel with specific real-world examples and models.

Simple Graphs

Degree Distribution The Königsberg bridge network had only four nodes; the network examples we cite nowadays have from hundreds to millions. Most of them show a degree heterogeneity best captured by the degree distribution, which carries more information than the average degree, as pointed out by Barabási and Albert (1999). Examples of scale-free networks include networks of metabolic reactions (Jeong et al. 2000), genetic regulatory interactions (Milo et al. 2002; Shen-Orr et al. 2002; Thieffry et al. 1998), earthquake event correlations (Baiesi and Paczuski 2004), word co-occurrence and synonyms (Dorogovtsev and Mendes 2001b; Ferrer i Cancho and Solé 2001; Motter et al. 2002; Sigman and Cecchi 2002), power lines (Albert et al. 2004; Watts and Strogatz 1998), air routes (Amaral et al. 2000; Barrat et al. 2004), the Internet (Broida and Claffy 2001; Faloutsos et al. 1999; Govindan and Tangmunarunkit 2000), the World Wide Web (Adamic 1999; Adamic and

Huberman 2000; Albert et al. 1999; Kleinberg et al. 1999; Kumar et al. 1999), software systems (Myers 2003), Wikipedia links (Capocci et al. 2006), phone calls (Aiello et al. 2000), e-mails (Ebel et al. 2002), coauthorship (Barabási et al. 2002; Newman 2001b), scientific citations (Redner 1998), World trade (Serrano and Boguñá 2003), innovation flow (Di Matteo et al. 2005), sexual partnership (Liljeros et al. 2001) and the list goes on.

Barabási and Albert had a much shorter list of examples to work with in 1999. Nonetheless, they saw that three very different networks, the actor network, power grid and World Wide Web had similar degree distributions, different from that of a random network model. They argued that the Erdős–Rényi random network model lacks two important features present in real-world systems. First, it is a static model, while most real-world networks constantly evolve and grow. Second, the random network model is too democratic: the probability of linking any two nodes is constant. Barabási and Albert proposed that in real networks the nodes that already have a large degree are more likely to receive new links as the network grows (think of Google in the WWW network). Preferential attachment accompanied by network growth was the first mechanism ever reported to reproduce the scale-free (power-law) degree distribution seen in real networks. Interestingly, though, Barabási and Albert were not the first to report it. A sociologist named Price reported the first example of a scale-free network back in 1965, that of citations linking scientific papers (de Solla Price 1965). Building on the “the rich get richer” idea proposed to explain wealth distributions, Price constructed a network model for citations in which the more citations a paper has, the more likely it is to acquire further citations (de Solla Price 1976).

The scale-free model, simple and analytically solvable, propelled scale-free networks and preferential attachment to the forefront of the expanding field of complex networks research. Barabási and Albert showed that both growth and preferential attachment are essential for obtaining a scale-free network. Growth along with uniform attachment leads to an exponential

degree distribution, while no growth with preferential attachment leads to a Gaussian distribution (although the system does start out with a transient power law) (Barabási et al. 1999). They also considered the effects of random rewiring and internal link formation, showing that internal link dynamics cause deviation from the power-law at low degrees, observed in real-world networks (Albert and Barabási 2000). A variety of models and analytical methods were developed in the wake of these papers, addressing the effects of further changes in rules of growth or attachment on the degree distribution. The exact solution for the degree distribution of the Barabási–Albert model was worked out by graph theorists Bollobás and Riordan (Bollobás et al. 2001).

One of the most important generalizations of the original scale-free model was the study of nonlinear preferential attachment by Krapivsky and Redner (Krapivsky and Redner 2001; Krapivsky et al. 2000). They found that power-law scaling is destroyed by nonlinearity: sublinear attachment leads to a power law multiplied by a stretched exponential, while faster than linear attachment causes the network to “condense”: the fraction of nodes connected to a single super-hub is finite in the thermodynamic limit. Indeed, the simple linear attachment rule of the scale-free model was later verified in real systems: citation networks, the Internet, the actor and scientific collaboration networks (Jeong et al. 2003; Newman 2001a).

Variations on the scale-free model include linear preferential attachment offset by a constant (Dorogovtsev et al. 2000), internal edge creation and removal (Dorogovtsev and Mendes 2000; Krapivsky and Redner 2002), growing average degree (Dorogovtsev and Mendes 2001a) (seen in the WWW and co-authorship networks Barabási et al. 2002), and edge rewiring (Albert and Barabási 2000; Tadić 2001). One of the challenges of modeling the WWW with the original scale-free model was spotted by Adamic and Huberman: while the oldest nodes are the ones with the highest degree in the model, the WWW does not show this correlation (Adamic and Huberman 2000). Bianconi and Barabási proposed a multiplicative fitness model (Bianconi

and Barabási 2001a) in which the attachment rule is influenced by the degree as well as the “worth” of a node. This model generates both scale-free networks and “winner takes all” scenarios; the transition between the two outcomes maps beautifully onto a Bose-Einstein condensation (Bianconi and Barabási 2001b).

The presence of preferential attachment can be justified in many real systems such as the WWW, citation, collaboration or airport networks through the larger visibility of high-degree nodes and the advantage nodes gain by linking to them. There are, however, scale-free networks where a different mechanism leading to preferential attachment is necessary. Biological networks offer intriguing examples: the metabolic and the protein-protein interaction networks are scale-free, even though their connections are governed by biochemistry and not choice. Protein interaction networks have inspired a class of models based on gene duplication (duplication of a node and all its links) and subsequent mutation (addition and/or deletion of some of the copy’s links) (Solé et al. 2002; Vázquez et al. 2003). Preferential attachment in these models is a consequence of the evolutionary dynamics: nodes with a higher degree have more duplicating neighbors, thus receiving more links. Vertex (node) copying has been proposed as a possible mechanism for the growth of the WWW (Kleinberg et al. 1999) and auto-catalytic networks (Jain and Krishna 1998).

In the spirit of the Erdős–Rényi model, Bender and Canfield proposed an ensemble model for scale-free networks. The configuration model describes the group of all networks with a prescribed degree sequence (Bender et al. 1997). If the sequence is chosen from a power-law distribution, the resulting networks are naturally scale-free. However, the average properties of the ensemble carry no other characteristics intrinsic to evolving models (such as degree correlations or clustering). Moreover, the simple definition of the model makes it ideal for analytical approaches. Newman et al. used probability generating functions to calculate exact expressions for average path length and clustering in configuration networks. (They used a generalized definition: the ensemble of all networks with an ensemble of

degree sequences drawn from the same distribution.) (Newman et al. 2001). Many analytical results for scale-free networks were proven using the configuration model: they have asymptotically vanishing clustering coefficients (Davidsen et al. 2002) and they are ultra-small for the degree exponents measured on most real-world networks ($\gamma \in (2, 3)$): their average path length scales as $O(\log \log N)$ (Cohen and Havlin 2003).

Some real networks are embedded in physical space and have physical connections: brain networks, the power grid, the Internet, airport networks, streets, public transportation systems, highways and rivers. Some of the above examples (brain networks, streets, rivers) are missing from the list of scale-free networks: spatial constraints can be forbidding to the formation of hubs. Several studies with both preferential attachment and bias towards shorter links show that large length costs can destroy the scale-free nature of spatial networks (Barthélemy 2003; Manna and Sen 2002; Xulvi-Brunet and Sokolov 2002). Systems with fixed maximum link length, such as wireless networks in which the range of a particular device is much smaller than the physical size of the system are not scale-free. Conformation networks made of all physically allowed conformations of a system (a polymer or bead chain) are also homogeneous structures naturally embedded in an n -dimensional configuration space defined by the system’s degrees of freedom (Ravasz et al. 2007; Scala et al. 2001).

The distribution of nodes in space can also have great influence on network topology, as shown in a detailed study of the Internet by Yook et al. (2003). They found that the router density distribution is a fractal with the same dimension $D = 1.5$ as the population density distribution. They were able to mimic the topology of the Internet using a simple evolving model in which nodes are distributed according to a fractal distribution and incoming nodes connect to old ones using preferential attachment divided by some power of their distance. Interestingly, the only model parameters able to reproduce the internet’s topology were the ones actually measured for the real system: fractal dimension $D = 1.5$, linear preferential attachment and a probability of

connecting two nodes that is inversely proportional to the distance between them. A similar model was also successful in describing the topology of the world-wide airport network (Guimerà and Amaral 2004).

Paths on Networks, Small Worlds and Betweenness A networks' most basic function always requires some type of communication along its edges. Thus it is natural that average shortest paths, network diameter and local betweenness measures are of great interest to networks research. Erdős and Rényi proved that the diameter of their random network model scales as the logarithm of node number. Watts and Strogatz called such networks small worlds (Watts and Strogatz 1998), in tribute to the “small world phenomenon” in sociology: the idea that one can connect any two people on Earth by about six handshakes between mutual acquaintances. In 1967, an ingenious experiment by Milgram proved the existence of short paths of an average six hops between random people in the US, known as “six degrees of separation” (Milgram 1967). The small world nature and searchability of small-world networks allow movie lovers to find short chains of movies connecting their favorite actor to Kevin Bacon. Mathematicians (and networks researchers) play the same game on the co-authorship network: one's shortest path to Pál Erdős is called the Erdős number.

The small world model introduced by Watts and Strogatz is based on the idea that real networks are in between random graphs and regular lattices: they are highly clustered (as a regular lattice), but they also have shortcuts. The model is built starting with a regular low-dimensional lattice to which one adds (or rewires) a certain number of edges, shortcuts between distant parts of the lattice (Watts and Strogatz 1998). Watts and Strogatz showed that increasing the number of shortcuts turns regular lattices into random networks, moreover, a small number of shortcuts is sufficient for the small-world effect without destroying the high clustering coefficient of the original lattice (Newman and Watts 1999; Watts and Strogatz 1998). Most real networks display both characteristics of the small world model: short average path lengths and high clustering.

However, the small world model has a peaked degree distribution, thus the topology of real networks with scale-free degree distribution is fundamentally different from the ones generated by the model. The Barabási–Albert scale-free model, on the other hand, fails to account for the high clustering of most real networks.

Logarithmic or slower increase of the average path length was proved for a variety of network models (Bollobás and Riordan 2004; Bollobás and de la Vega 1982; Chung and Lu 2002). Bollobás and Riordan showed that the average shortest path length in scale-free networks grows no faster than $\log N / \log(\log N)$ (Bollobás and Riordan 2004). Cohen and Havlin used the configuration model to show that random scale-free networks with $\gamma \in (2, 3)$ are ultra-small: their average shortest path length grows as $\log(\log N)$ (Cohen and Havlin 2003).

The structure of shortest paths is crucial to any communication or flow between nodes of a network. Naturally, betweenness was found to be the relevant quantity when one deals with congestion or disruption of flow in networks. Goh et al. measured the distribution of node betweenness values for a variety of real networks as well as models, and showed that it follows a power-law with only two distinct exponents (Goh et al. 2002).

Clustering and Network Motifs Clustering is a rediscovery of “network density”, a quantity widely used in sociological network analysis: it provides a measure of how well one's acquaintances know each other. High values have been observed in social networks, but also in most other real-world networks, motivating the development of clustered scale-free models. The Holme–Kim model, aimed at creating scale-free networks that also have high clustering coefficients, is a straightforward generalization of the scale-free model, with triangle-forming steps complementing preferential attachment (Holme and Kim 2002a). Klemm and Eguíluz introduced a citation network model based on the idea that papers are only cited for a limited stretch of time before they are forgotten (Klemm and Eguíluz 2002). The model is built by the constant addition of nodes that connect to all “active” nodes and join their ranks. Then, one of the active nodes is deactivated with

a probability inversely proportional to its in-degree (offset by a constant). This model leads to scale-free networks with high clustering coefficient, but fails to capture their small-world nature: visualized, the networks look like tubes. Gene duplication models, while motivated by evolutionary arguments, also lead to clustered scale-free networks (Solé et al. 2002; Vázquez et al. 2003).

An interesting generalization of the clustering coefficient was introduced by Uri Alon's group: network motifs are significantly over- or under-represented patterns of connections between n vertices (compared to the randomly rewired network). Distinct characteristic motifs were found in regulatory networks, food webs, neural networks and WWW, corresponding to local functions performed by the network (Milo et al. 2002; Shen-Orr et al. 2002). For example, different types of feed-forward loops (FFLs, directed motifs of 3 nodes: $A \rightarrow B$, $B \rightarrow C$ and $A \rightarrow C$) in genetic regulatory networks perform distinct signal processing roles as shown by both simulation and experiments with living cells (Alon 2007). FFLs made of activating interactions only (abundant in the regulatory network) can filter out transient changes in the concentration of the input node, while also delaying the turn-on or turn-off of the output node. On the other hand, FFLs where the $B \rightarrow C$ link is a repressing one (also abundant) act as pulse generators.

Degree Correlations and Mixing Patterns

In social networks, links between people who are alike are more common; popular people are connected with popular people. Assortative mixing means that degrees at two ends of an edge are correlated, as measured by the conditional probability, $P(k'|k)$, that a node with k links is connected to another one with k' links. Measurements on the Internet and protein interaction networks show that in these systems, as opposed to their social counterparts, small degrees are more likely to connect to high degree nodes (Maslov and Sneppen 2002). The conditional probability is difficult to measure in most real networks due to poor statistics, although it is convenient in analytical work. A more compact representation of degree correlations was defined

by Pastor-Satorras et al. (2001): the average degree of neighbors as a function of degree, $k_{nn}(k)$, which decreases with k for disassortative systems. One can further simplify the measure of assortativity by calculating the Pearson correlation coefficient of degrees at the ends of a network's edges: the assortativity coefficient (Newman 2002a; Newman 2003). Intriguingly, most social systems are assortative (actor network, company directors, coauthorship networks, phone calls, email address books), while most technological and biological systems prefer disassortative mixing (WWW, Internet, train routes, software packages, software classes, electronic circuits, peer-to-peer networks, metabolic networks, food webs, neural networks).

Degree is not the only property of a network that can show assortative or disassortative mixing. In networks where nodes can be classified in types of some kind, mixing between types can also be characterized by the assortativity coefficient (see "Definition"). Maslov et al. showed that there are three main types of nodes in the Internet: high level providers who manage the backbone and trunk lines, Internet Service Providers who bring the network out to end-users and the end-users themselves. These three types show strong disassortativity: few end-user to end-user or ISP to ISP links in the network. In social networks, mixing by race, age or income has been observed (Newman 2003).

Communities, Hierarchy and Fractality

Community structure is an intuitive feature of complex networks: one expects them in social systems (circles of friends), biological networks (functional units), the WWW (websites related to a topic or organizations), co-authorship networks (scientific fields and sub-fields), etc. Communities within networks are structural features related to the function of the network as a whole, and are thus expected to have a strong influence on their dynamics. Defining and finding network communities has its history in both sociology and computer science, and has been revisited many times. The methods developed along the way paint a rich picture of the structural diversity of complex networks.

Non-Overlapping Community Structure

Hierarchical clustering or cluster analysis is

widely used in the study of social networks. The first step in hierarchical clustering is the construction of a similarity measure between network nodes. Next, each node is assigned to a separate cluster (the leaves of the dendrogram). The two most similar clusters are joined to form junctions of the dendrogram, until all clusters have been united, forming the root. Many similarity measures have been defined and used successfully. Structural equivalence, used in social network analysis, gives two nodes the highest similarity score if they have the same pattern of relationships. It can be measured using Euclidean distance or Pearson correlation coefficient between rows of the adjacency matrix, as well as topological overlap, defined as the number of overlapping neighbors divided by the smaller of the two degrees (Ravasz et al. 2002).

Girvan and Newman introduced a famous community detection algorithm that is similar to hierarchical clustering, but works divisively (Girvan and Newman 2002). It is based on the idea that the edges most likely to run between communities are the ones that have the highest edge betweenness centrality. They first remove the edge with the highest betweenness, then recompute edge betweenness and keep removing edges until the network falls apart into non-connected nodes. As the network falls apart, they draw a dendrogram where each joint is a splitting event.

Hierarchical clustering works with varying success for different systems, but it cannot determine how many communities there are in the network. Newman et al. introduced an elegant measure for the “quality” of any given partitioning into communities, called modularity, which compares a community partitioning to a null model that can be appropriately chosen for the system at hand (Newman 2006). The Girvan–Newman algorithm, together with the dendrogram cut that maximizes modularity, has been successfully used for many different social and biological networks (Arenas et al. 2004; Boguñá et al. 2004; Guimerà et al. 2003; Newman and Girvan 2004; Tyler et al. 2003; Wilkinson and Huberman 2004). The main drawback of the method is computation time ($O(N^3)$ on a sparse graph): it is not feasible for networks with more than a few thousand nodes.

In a quest to develop a faster community detection method closely tied to the definition of communities, Newman used direct optimization of the modularity measure (Newman 2004). Since finding the best partitioning is an NP-hard problem, his first approach was a greedy optimization. All nodes start out as separate communities, which are then repeatedly joined such that the increase in modularity is maximal (or decrease is minimal). Newman showed that the method works well both in tests and real networks, and it works quite fast: $O(N^2)$ time for sparse graphs. Still not fast enough? A collaboration with Clauset and Moore resulted in an algorithm that performed the same optimization in $O(N \log^2 N)$ for sparse graphs with many levels of communities (Clauset et al. 2004), solving the problem of partitioning networks with billions of nodes. (The general result for runtime is $O(KD \log N)$, where K is the total number of links and D is the depth of the generated dendrogram).

Interested in the theoretical foundations of community structure detection and its relationship to matrix spectra, Newman argued that community detection requires the use of the modularity matrix (Newman 2006) in place of the Laplacian matrix, as done by traditional spectral methods of graph partitioning. (The Laplacian matrix of a graph, L , is a real symmetric matrix with elements $L_{ij} = k_i \delta_{ij} - A_{ij}$) The modularity matrix is defined as $B_{ij} = A_{ij} - P_{ij}$ (see “Modularity Definition”). He showed that the eigenvalues and eigenvectors of the modularity matrix encode the networks’ community structure. Methods based on this relationship perform as well, if not better, than previous ones, but more importantly, they are also able to detect “anti-modular”, or bipartite structure (Newman 2006).

Hierarchical Community Structure and Fractal Networks Ravasz et al. argued that in many real networks with interesting modular structure there is no ideal partitioning into distinct modules: the network is built of small, very cohesive communities, hierarchically embedded in larger, less cohesive ones (Ravasz and Barabási 2002; Ravasz et al. 2002). Their hierarchical model is a deterministic construction of a scale-free network with hierarchically embedded modules. They showed

that hubs on all scales unite communities on all scales: small nodes are part of small, very cohesive clusters (thus have large clustering coefficients), larger nodes serve as connectors of these clusters, while the largest hubs span modules at the highest level or organization (and have low clustering coefficients). Indeed, they found that the clustering coefficient $C(k)$ decreases with increasing k in a variety of real networks, such as the metabolic network, synonyms, movie actors, the WWW and the Internet represented at Autonomous System level (each node is a domain, not just a computer), and it often scales as $1/k$ (Ravasz and Barabási 2002). This scaling was found in a variety of other networks: software systems (Myers 2003), the World Trade network (Serrano and Boguñá 2003), the worldwide airport network, the co-authorship network of <http://arxiv.org/archive/cond-mat> (Barrat et al. 2004; Newman 2001b) and protein folding networks (Rao and Caffisch 2004). Not all networks are hierarchical: the power grid and the Internet at router level show no scaling of the clustering coefficient (Ravasz and Barabási 2002). Ravasz et al. suggested that spatial embedding of both systems, where length costs are significant, works against hierarchical modularity. Both networks distribute something to a physical area. Thus, the formation of tight communities is not required for these networks to function.

Hierarchical organization in metabolic networks was found to reflect biological function on different scales of organization: the branches of the dendrogram obtained by hierarchical clustering (using topological overlap as similarity measure) correspond to known functional classes of the metabolism on two different levels of organization (Ravasz et al. 2002).

The question of self-similarity or fractal nature has been on the mind of network researchers since the scale-free degree distribution was observed. Are networks like fractals, self-similar on all scales? Hierarchical organization strengthens this image: most networks not only have degrees in a broad range of scales, they are also made of modules of different scales embedded into each other. The problem with complex networks as fractals was, of course, that most networks of interest to us

are also small-world (Watts and Strogatz 1998). In a small-world network the number of nodes at a distance l from any given node increases exponentially. One expects this number to grow as a power law in the case of a fractal object: measuring the “mass” within distance l from a point on the object, called the cluster growing method, is one way of measuring fractal dimension.

While some deterministic models have been constructed with the idea of fractality in mind (Dorogovtsev et al. 2002; Jung et al. 2002), the breakthrough in understanding topological self-similarity in complex networks was brought forth by Song, Havlin and Makse (Song et al. 2005; Song et al. 2006). They generalized the standard box counting method for measuring fractal dimension of a physical object to complex networks. How does one cover a network with boxes of different size? Divide all nodes in groups such that the shortest path between any two nodes in a group is at most l_B long: these are the boxes. Use the smallest number of groups necessary to do this (or a decent approximation) and repeat it for $l_B \in [2, D]$. The results of this procedure were quite surprising: many scale-free real-world networks, such as the WWW, actor network and various metabolic networks show a neat fractal scaling between the number of boxes and their size. Thus these networks are self-similar, fractal structures. To prove their point further, the authors used a renormalization procedure where they collapsed each box into a node and linked these new nodes to each other if any member of the original boxes had a connection. The networks renormalized this way were also a scale-free, with the same degree distribution exponent, independent of the box size used for renormalization (Song et al. 2005).

The question of how these networks are small world and self-similar at the same time has also been resolved: the two methods of determining the fractal dimension of an object, box counting and cluster growing are not equivalent on complex networks with broad degree distribution. While box counting covers all the hubs only once (they are assigned to one box only), cluster growing finds the hubs for almost any choice of seed node, thus bringing a large part of the

network into the cluster with them. This explains the exponential increase in the number of nodes within a distance l , and shows the small-world property of the system. Box counting, on the other hand, can reveal the fractal nature of the network, if present (Song et al. 2005).

Song et al. uncover some of the requirements of fractality via proposing a network growth model based on reverse renormalization. Starting from one point, the network grows by nodes transforming into small clusters in each iteration. The conversion from a node to a small cluster mimics the renormalization process in reverse: the degree of a node grows by multiplication with a scaling factor (thus nodes of previous iterations become the hubs). The newly formed clusters have a diameter of b_B (the box size). They showed that the key feature that influences fractality in the emerging networks is how the clusters connect: if the link always runs between the hubs (leading to assortative mixing), the result is small-world network that is not a fractal. The internet at router level, found to be non-hierarchical, is a good example of such an assortative, non-fractal network. On the other hand, if the clusters only connect to each other via the non-hub (newly created) nodes, the resulting network is a fractal, but it loses its small-world character. Many real-world networks, however, seem to be both fractal and small-world (WWW, actor network, protein interaction networks, metabolic networks). Indeed a very small number of hub-to-hub connections in this model can restore the small-world property of the network while preserving its fractal nature.

Overlapping Community Structure The community detection methods presented thus far assign each node to only one community. Palla et al. argued that many nodes in real networks belong to more than one community (Palla et al. 2005): proteins can simultaneously be part of several complexes, people have disjoint groups of acquaintances from friends to work to extended family. They proposed a community definition that allows them to capture overlap between communities. Their method is based on “ k -clique rolling”: a k -clique community is the union of all k -cliques (complete subgraphs of size k) that can be connected through a series of k -cliques that

share $k - 1$ nodes. Increasing values of k lead to smaller, denser, but more disjoint communities. They find that k -clique communities in real networks (co-authorship, word association and protein interaction networks) have a power-law size distribution, and there are significant overlaps: the size distributions of overlap as well as node membership have fat tails.

Directed Networks

Directionality of a link is often important in real networks: scientific citations, url links, genetic regulatory interactions are only a few examples of inherently asymmetric connections. Directed links require the separate measurement of in- and out-degree distributions. In case of the WWW both are power-laws, but the degree exponents differ: $P_{\text{in}}^{\text{WWW}}(k) \sim k^{-2.1}$ and $P_{\text{out}}^{\text{WWW}}(k) \sim k^{-2.45}$ (Albert et al. 1999). Genetic regulatory networks show an even stronger difference. Their out-degree distributions are power laws, however, the in-degree ones are scaled: genes cannot receive input from hundreds of transcription factors.

Another interesting consequence of directed links is the rich structure of directed paths. They were found to partition the WWW as well as metabolic networks into parts resembling a bow-tie (Broder et al. 2000; Ma and Zeng 2003): a strongly connected component, in which there is a directed path in both directions between any pair of nodes, an IN-component, the nodes of which can reach the strongly connected component but cannot themselves be reached, and an OUT-component that can be reached from, but has no directed paths leading into the strongly connected component. Not all directed networks have bow-tie structure: some of them are entirely acyclic, with no directed loops. Citation networks are a natural example: one can only cite papers already published. However, genetic regulatory networks are also acyclic (not considering auto-regulatory loops), even though the cause of this is now yet understood (Balázsi et al. 2005; Thieffry et al. 1998).

Gradient networks are directed graphs that generalize the concept of gradients from continuous scalar fields to networks. They capture the backbone of a gradient-induced flow on complex networks: given a substrate graph with a scalar value

associated to every node, its gradient network is formed by the collection of all directed links that lead from every node to its neighbor with the highest scalar value (Toroczkai and Bassler 2004). These directed links form collections of trees. For an independent, identically distributed association of random variables to the nodes of an Erdős–Rényi graph, the generated gradient network has been shown to be scale-free, with a connectivity exponent of $\gamma = -1$. This finding can be proved for any substrate graph with no loops shorter than 5 (Toroczkai et al. 2004). Moreover, the gradient networks' scale-free nature seems to be universal: it was numerically observed for a wide variety of substrate networks (including ones with short loops): regular and random trees, Erdős–Rényi and small-world networks, high dimensional regular lattices and n -tori, random geometric networks (Dall and Christensen 2002), the scale-free and the configuration model (Ravasz et al. 2007; Toroczkai et al. 2004).

Weighted Networks

Real world networks display significant heterogeneity in the strength of their connections. The distribution of link weights has been found to have a heavy tail in metabolic networks: the steady-state flux distribution follows $\Theta(w) \sim (w_0 + w)^{-1.5}$ ($w_0 = 3 \cdot 10^{-4}$) (Almaas et al. 2004). Moreover, the average link strength scales with the connectivity of the nodes at the two ends as $\langle w_{ij} \rangle \sim (k_i k_j)^{0.5}$ in both metabolic networks and the Worldwide Airport Network, indicating correlations between node degree and links weights (Almaas et al. 2004; Barrat et al. 2004). Scientific collaboration networks, on the other hand, have a weight distribution that is not correlated with degree.

The existence of weighted links requires a generalization of most network measures:

- **Node strength and strength distribution.** Node strength, s_i is a natural generalization of the node degree, k_i :

$$s_i = \sum_{j=1}^N w_{ij} A_{ij},$$

the sum of weights over the links of node i . The strength distribution, $P(s)$, is typically also heavy

tailed (Barrat et al. 2004). Weights are often dependent upon topology (see “Metabolic and Airport Networks”), expressed by a nonlinear relationship between node strength and degree: $s \sim k^\beta$ (in the airport network $\beta = 1.5$). Heterogeneity in the weights around a node can be measured using

$$Y_i = \sum_{j=1}^N \left(\frac{w_{ij}}{s_i} \right)^2 A_{ij}.$$

If all edges have the same weight, $Y(k)$ scales as $1/k$, while if one weight is significantly larger than the others, $Y(k) \simeq 1$. In metabolic networks $Y(k)$ was found to scale as $k^{-0.27}$, indicating that metabolites used in a large number of reactions are more likely to have one high-flux reaction dominating their production (consumption) (Almaas et al. 2004).

- **Weighted clustering coefficient.** Defined by Barrat et al. as

$$C_i^W = \frac{1}{s_i(k_i - 1)} \sum_{j=1}^N \sum_{m=1}^N \frac{w_{ij} + w_{im}}{2} A_{jm} A_{ij} A_{im},$$

the weighted clustering coefficient is often compared to the standard one: $C^W > C$ means that the triangles of the network are preferentially formed by high-weight links. This is indeed the case in the coauthorship network, for nodes with $k > 10$: more established investigators form stable, high-weight cliques (research groups) from which the main volume of their publications originate. A similar phenomenon can be seen in the world-wide airport network: larger airports form high passenger-flux triangles, so called “rich-clubs” (Barrat et al. 2004).

- **Degree Correlations.** The weighted average degree of neighbors is defined as:

$$k_{nn,i}^W = \frac{1}{s_i} \sum_{j=1}^N w_{ij} k_j A_{ij},$$

a sensitive probe into the structure of weighted networks. The behavior of $k_{nn}(k)$ in the airport

network shows a plateau for airports with more than 10 direct flights, indicating no degree preference. However, $k_{nn}^w(k)$ increases in a wider range and is in general larger $k_{nn}(k)$, showing that while large airports do not preferentially connect to large airports, the high traffic links run among members of the “rich-clubs” (Barrat et al. 2004).

Dynamics on Complex Networks

The main theme of this section is: how does the structure of a network influence its dynamics? Most lessons of statistical mechanics are worth revisiting when the underlying space is a network: does an inhomogeneous topology change the dynamics? The answer, as we will see, is yes, in interesting ways.

Robustness and Vulnerability of Complex Networks

Perhaps the most intriguing feature of complex systems is their robustness. Close to 75% of the genes in *E. coli* are non-essential: the organism can survive without them (under one set of growth conditions) (Gerdes et al. 2003). If the webpage of a company or university goes down, the WWW as a whole is still perfectly functional, the effect of the failure is local. On the other hand, an intentional “attack”, similar to the denial-of-service attacks that crippled Yahoo, Amazon, eBay, CNN and a few other very popular websites in February of 2000, can substantially cripple the function of a complex system.

Vulnerability and robustness go hand in hand in most complex systems: bad weather in Atlanta (although usually not labeled an “attack”) has very different consequences for air traffic than problems at a regional airport. Opinions expressed in the New York Times are much more likely to spread and influence events than opinions in a small town local newspaper. These trivial examples hint at interesting consequences of in-homogeneous network topology, brought to light in a 2000 Nature paper by Albert et al. (2000): while scale-free networks are largely unaffected by random failure, they are very sensitive to change in their highly connected, central nodes, rendering them vulnerable (and/or responsive) to planned, targeted interventions.

Resilience One of the simplest indicators of robustness under the damage done by node or link removal is a structural one: the size of the largest connected component. Numerical studies performed by Albert et al. show that the giant connected component of Erdős–Rényi random networks falls apart at a much lower fraction of randomly removed nodes than of a scale-free network (Albert et al. 2000). A fraction of nodes the removal of which causes a random network to fall into pieces, only slightly shrinks the giant component of a scale-free network, while small fragments of the system become isolated. An attack, on the other hand, where the most connected nodes are the first to be removed, shows a different picture. While the Erdős–Rényi random network falls apart somewhat faster but in essentially the same way, a scale-free network is blasted apart by the removal of a much lower fraction of nodes. The results hold for simulations using the actual network topologies of the Internet and WWW (Albert et al. 2000; Broder et al. 2000).

The topological aspects of random node or edge removal can be calculated by mapping random failures to percolation problems. Cohen et al. have shown that uncorrelated random networks with a diverging second moment of their degree distribution (scale-free networks with degree exponents between 2 and 3) have zero percolation thresholds (Cohen et al. 2000). Vázquez and Moreno used an approach that allowed them to investigate the percolation properties of correlated networks, showing that assortative mixing is beneficial for resilience: it can push the percolation threshold down to zero, even for networks with a finite second moment (Vázquez and Weigt 2003). The opposite effect is also true: scale-free networks with diverging second moments but disassortative degree correlations are less resilient to node failure (Leone et al. 2002). A general analytical approach based on generating function formalism not only reproduced the previous results, but also allowed Callaway and Newman to investigate degree-dependent node removal scenarios, such as attacks (Callaway et al. 2000). Interestingly, assortative mixing does not help in case of an attack: Song et al. have found that non-fractal networks created via a mechanism that

favors hub to hub connections on all scales are more vulnerable to intentional attack than their fractal (and also disassortative) counterparts (Song et al. 2006).

Cascading Failures The function of a variety of complex networks involves the transmission or flow of some conserved quantity. Removal or failure of a node in such a network has consequences that ripple through the rest of the system far beyond the effects on connectivity: the node suddenly sheds the load or flux that it carried before, thus its neighbors suddenly experience higher loads: some of these overload and fail. A cascading failure can follow, as often seen on the power grid, perhaps the most quoted example of the phenomenon. Unlike the fragmentation of a network, a cascading failure can be triggered by a relatively small number of node failures, often a single one (Holme and Kim 2002b; Motter and Lai 2002).

Using a model of overload in which the load-bearing capacity of a node is proportional to its load (betweenness) in the full network, Motter and Lai showed that scale-free networks are more vulnerable to randomly seeded cascading failures than random networks (Motter and Lai 2002). The vulnerability becomes especially pronounced under targeted attack: overload of the largest node can cause cascades that propagate through the whole system. They find that the most dangerous targets are not the most highly connected, but the most load-bearing (highest betweenness centrality) nodes. Betweenness is usually correlated with degree. The US powergrid, however, is vulnerable under attack targeting its most central nodes, but not its highest degree ones.

In a followup paper Motter introduced a fast defense strategy against cascading failures (Motter 2004). He argued that the only defense strategy which is fast enough is further removal of nodes: counterintuitive, but effective, if the nodes are carefully chosen. The reason this is possible, he argued, is because nodes that carry small amounts of load (thus are less central to the network) actually generate much more load than they carry. Their shortest paths to the rest of the system are larger, thus all the communication (traffic, power) they receive or generate affects a larger

number of intermediary nodes, increasing the total network load. Generated and handled load are anticorrelated, thus removal of nodes in ascending order of loads significantly reduces the size of cascading failures in the rest of the network, as verified by numerical simulations.

Congestion Cascading failures and congestion of traffic carried by networks are similar problems. As opposed to the node-removing effect of a failure, congestion does not disconnect a node, nonetheless, it can bring the traffic-bearing capability of a system to a halt. Most congestion models show a transition from free flow to congestion as the load is increased, regardless of the network type.

Ohira and Sawatari showed the occurrence of a jamming transition on a simple traffic model in which packets travel along the shortest paths of a two dimensional lattice between randomly chosen boundary nodes (Ohira and Sawatari 1998). On a regular lattice shortest paths are highly degenerate, thus the authors considered two strategies: one is deterministic in picking its route, the other is random, preferring shortest paths but occasionally picking longer than optimal ones. They found that the jamming transition occurred at larger packet creation rates if the routing was probabilistic, with an optimal randomness that does not considerably lengthen the travel paths, but relieves the network from always choosing congested paths. Guimerà et al. considered a different formulation of the congestion problem on lattices and Cayley trees where all nodes generate packets to random destinations and send them along shortest paths, but the probability for a packet to hop between two nodes along the path depends on the queues accumulated by these two nodes (Guimerà et al. 2002). Thus, there is some congestion-awareness built into the model. If the processing speed of nodes decreases with an increased number of packets, the system shows a discontinuous transition from free flow to congested state: the ratio of undelivered packets (the order parameter) jumps from 0 to 1. The positive feedback between congestion and slower processing leads to the formation of congestion nuclei that spread through the network. On the other hand, no transition is observed in networks

in which the processing speed of nodes increases with queue lengths, only a crossover from low-density flow to high density flow accompanied by a change in fluctuation statistics. The critical case in between is queue-independent processing, which shows a continuous transition between free flow and congestion.

Solé and Valverde proposed a generalization of the Ohira–Sawatari model (Solé and Valverde 2001) and showed that the system at transition point exhibits self-similar time-series dynamics with an $1/f$ power spectrum, as observed in measurements of packet transmission times on the Internet. Latency times and queue lengths also showed heavy tails with similar queue length distributions to jam size distribution in highway traffic models. Interestingly, the system reaches its highest efficiency and information transfer regime right at the critical point, before entering the congested state (Solé and Valverde 2001).

Building on the observation that the time series dynamics of the model close to the critical point matches the real data, the authors introduced a self-organizing version of the model (Valverde and Solé 2002). They argued that packet generation (thus user behavior) is linked to dynamics: each user tries to increase its rate until congestion of neighboring nodes is detected, at which point it starts to decrease it, dropping its rate to 0 if all its neighbors are congested. This model generates highly heterogeneous dynamics in space and time, with a power-law congestion length distribution. Moreover, this model points to internal network dynamics being responsible for fluctuations, supported by an analysis of real fluctuations by de Menezes and Barabási. They observed a power-law scaling of flux fluctuations as a function of total flux values, with two distinct scaling exponents. $\alpha = 1/2$ scaling is generated by fluctuations internal to the system (as seen in the Internet and on a microchip), while $\alpha = 1$ corresponds to external noise (seen in the WWW, river networks and the highway system) (de Menezes and Barabási 2004). Solé and Valverde have further extended their model to study complex topologies similar to the Internet (using the model by Yook et al. 2003), with a routing strategy that can be tuned from random routing to global shortest path

routing. Each node is assumed to know its neighborhood to m hops. If the destination of a packet is within a node's search horizon it uses shortest path routing, otherwise it passes the packet to a random neighbor (Valverde and Solé 2004) (local routing strategies with a fixed search horizon were also investigated by Tadić et al. (Tadić and Rodgers 2002; Tadić and Thurner 2004)). They found that the routing was optimal when the search horizon equaled the average path length of the network. Further push toward global shortest paths actually decreased the efficiency by over-specifying paths and thus exacerbating congestion. The dynamics observed with optimal search depth reproduced the $1/2$ scaling between fluctuations and mean flow observed in (de Menezes and Barabási 2004), as well as the power-law exponent of the average latency time distribution measured on the Internet.

Zhao et al. investigated the effect of network topology on congestion in a model in which the packet processing speed of nodes is determined by their degree or their betweenness. They found that if the capacity of nodes was proportional to their degree, random networks as well as scale-free ones were less prone to congestion than regular lattices or Cayley trees. However, systems in which the node capacities were proportional to their betweenness had the same critical packet generation rate regardless of topology, suggesting that selectively increasing the capacity of high-betweenness nodes is a good way of increasing the carrying capacity of the system as a whole (Zhao et al. 2005).

A different approach for investigating the effect of network topology on congestion was proposed by Toroczkai and Bassler (2004). They measured the congestion factor of the Erdős–Rényi and Barabási–Albert models, defined as the average fraction of nodes that do not receive and thus process incoming traffic. Instead of an explicit choice of routing or packet generation behavior, they assumed that packets on average follow the steepest gradients towards the neighbor with the highest “potential”, thus the gradient links determine the congestion factor (they assume a random distribution of node potentials). They found that the congestion factor of Erdős–

Rényi random graphs increases with the size of the network, asymptotically growing to 1, while for scale-free networks it quickly reaches a value of ~ 0.7 and does not increase with system size. A followup study by Danila et al. proposed a traffic model based on the idea of congestion-gradient driven flows (Danila et al. 2007).

The recognition that congestion occurs when the average number of packets processed by the busiest node reaches 1 (time-step) highlighted the importance of betweenness in the study of congestion. Routing protocols can influence the experienced betweenness of a node: the number of packets that actually go through it on average. Several methods of reducing the largest betweenness value have been investigated: optimization of link weights such that the shortest weighted paths give rise to a small maximum betweenness (Danila et al. 2006), hub avoiding global routing Schemes (Sreenivasan et al. 2007) or traffic-aware routing (Echenique et al. 2004). Sreenivasan et al. proved that for any network topology there always exist an absolute upper bound for the communication threshold, determined by network topology, above which no routing algorithm can increase the critical congestion threshold (Sreenivasan et al. 2007).

Spreading Processes and Social Dynamics

Epidemic Models Epidemiological modeling jumped to the forefront of networks research with a landmark paper by Pastor-Satorras and Vespignani which revealed the striking difference between virus spreading on scale-free networks and homogeneous systems (Pastor-Satorras and Vespignani 2001a, b). They studied the “susceptible–infected–susceptible” (SIS) epidemic model, suited to describe diseases that confer no immunity, such as tuberculosis, gonorrhea as well as computer viruses on systems that do not update their virus protection software. Each susceptible node can be infected with rate ν if it is connected to one or more infected nodes, while infected nodes are cured with rate δ and become susceptible again. The SIS model was known to show a non-equilibrium phase transition at a critical spreading rate λ_c ($\lambda = \nu/\delta$): if the spreading rate is higher than this threshold, the disease is

endemic; a finite fraction of nodes is persistently infected. Below the threshold the disease dies out completely after an initial breakout. As Pastor-Satorras and Vespignani pointed out, these results were obtained on lattices and failed to explain the very low but sustained prevalence of computer viruses. The authors report the absence of a critical point on scale-free networks with $2 < \gamma \leq 3$: there is no non-zero spreading rate for which the disease dies out. As λ approaches 0, the prevalence of the disease decreases exponentially, but only reaches 0 when $\lambda = 0$.

In a followup study together with Moreno they showed that the lack of an epidemic threshold holds for the “susceptible–infected–recovered” (SIR) model as well (Moreno et al. 2002). This model, applicable for diseases that result in immunity or death, has a radically different overall behavior from the SIS model. Recovered individuals cannot get infected again, thus the disease always dies out. Nonetheless, for homogeneous networks it shows a phase transition at a critical spreading rate λ_c , reflected in the total fraction of the population to ever get the disease. Below λ_c this fraction is vanishing as the system size goes to infinity, above λ_c there is a finite infected fraction. Moreno et al. have found that the critical spreading rate for uncorrelated complex networks is $\lambda_c = \langle k \rangle / \langle k^2 \rangle$.

Thus, networks with diverging connectivity fluctuations (such as scale-free graphs with $2 < \gamma \leq 3$) have no non-zero epidemic threshold. Although real and thus finite-size networks cannot have infinite $\langle k^2 \rangle$, the epidemic threshold is very small for large systems, much smaller than that of a similar homogeneous network, and it decreases with systems size (Pastor-Satorras and Vespignani 2002a). The SIR model has been mapped onto a bond percolation problem by Grassberger (1983). This mapping was exploited by Newman, who used the generating function formalism (Callaway et al. 2000; Newman et al. 2001) to obtain the exact solution of the model in the infinite time limit for simple graphs with arbitrary degree distribution. He then extended the mapping to bipartite graphs to model sexually transmitted diseases spreading between men and women (Newman 2002b).

The absence of an epidemic threshold has profound implications on immunization policies effective in scale-free networks. Dezső and Barabási (2002) as well as Pastor-Satorras and Vespignani (2002b) have shown that scale-free networks do not respond to random immunization: such a strategy cannot restore the epidemic threshold, or bring the effective spreading rate below it, even for an unrealistically high number of administered vaccines. On the other hand, immunization preferentially targeting the hubs of the network successfully reintroduces an epidemic threshold at very low vaccination rates, even if the strategy is imperfect in identifying the hubs. These results have important and controversial consequences for public policy of vaccination in the context of sexually transmitted diseases. This is partly because a policy that gives priority vaccination to prostitutes is controversial even if the public benefits are substantial, but also because it is generally difficult to identify the hubs of sexual networks. Cohen et al. proposed an immunization policy that overcomes this problem without relying on any global knowledge of the system: immunize a randomly chosen friend of a random person (Cohen et al. 2003). They showed that this strategy preferentially targets the hubs, thus restoring the epidemic threshold.

Epidemic spreading on networks with degree correlations show that degree correlations do not affect the lack of epidemic threshold in scale-free networks (Boguñá et al. 2003; Moreno et al. 2003). However, the epidemic incidence is smaller in these networks, while diseases are longer lived (Moreno et al. 2003).

The influence of link weights on epidemic spreading has been investigated in the context of diseases such as Severe Acute Respiratory Syndrome (SARS), spreading on the world-wide airline network (Colizza et al. 2006). Colizza et al. developed a detailed multi-scale model of global epidemic spreading and found that the degree heterogeneity of the airport network accounts for most of the observed behavior of the epidemics, the heterogeneity of its weights has a much smaller influence on the spread of the disease (Colizza et al. 2006). They found that epidemics

are fairly predictable, except at the very beginning of an outbreak originating from a hub, as well as the end of epidemics (Colizza et al. 2006).

Information Spreading The similarity between rumor spreading and epidemic spreading was recognized as early as 1964, when Goffman and Newill used the SIR model to describe the spread of ideas instead of diseases (Goffman and Newill 1964). The authors pointed out an important difference between the two processes: while one studies epidemic models with an effective immunization strategy in mind, information spread is in general favored; moreover, the process can be engineered in a way that facilitates high reliability of the spread. Later in the same year, Daley and Kendall published a spreading model that is specific to rumor (or information) spreading: instead of the random recovery rate of the SIR model (which assumes spontaneous forgetting of the news), they assumed that nodes lose their interest in spreading the news upon encounter with another node that knows it (Daley and Kendall 1965). Thus the “recovery” process of the Daley–Kendall model is very different from that of SIR, leading to a significant difference in the outcome of spreading. Assuming homogeneous mixing (each infected individual, or spreader can randomly contact any node in the system), the final fraction of nodes who have heard the news is ~80%.

A decentralized, spontaneous and robust method of spreading information was welcome by the computer science community; it allowed them to overcome the scalability problems of data disseminating protocols in large-scale distributed computing (Vogels et al. 2003) and peer-to-peer networks (Kermarrec et al. 2003). It was also used in update management of databases duplicated at many sites (Demers et al. 1987).

In the context of complex networks, the Daley–Kendall model was first investigated on the small-world model by Zanette, who found that below a density of shortcuts the rumor dies out without reaching a finite fraction of nodes (Zanette 2001). Moreover, this threshold is finite for infinite systems ($p_c = 0.2$ for $K = 2$), even though the network is turned into a small-world by a vanishingly small number of shortcuts.

Moreno et al. studied the same model on homogeneous versus scale-free networks and found that as opposed to epidemic spreading, rumors spread to a higher fraction of nodes in homogeneous networks (Moreno et al. 2004). Hubs in scale-free networks have a conflicting effect on rumor spreading: while they are highly likely and quick to hear the information, they also facilitate the formation of stifer nodes who do not spread the rumor.

Searching on Complex Networks

Milgram's famous experiment showing six degrees of separation between two random people not only showed the existence of short paths on social networks, it also highlighted the fact that finding a destination node with local information is not very difficult (Milgram 1967). Motivated by these findings, Kleinberg showed that the performance of a simple greedy search critically depends on the topology of the underlying network. He used a small-world type model in which nodes sit on a two-dimensional lattice (connected to their four neighbors) to which a few long-range connections are added. Unlike in the small-world model, these connections are not added entirely randomly: the probability of a shortcut is proportional to $r^{-\alpha}$, where r is the Manhattan distance between two nodes. In this model the best-case performance of a decentralized algorithm (the expected delivery time) scales as $(\log N)^2$ for $\alpha = 2$. However, both larger and smaller values of α result in expected times that scale as polynomials in N , highlighting that not all networks with short average path lengths allow the use of efficient decentralized searches (Kleinberg 2000).

Adamic et al. proposed to exploit the heterogeneous nature of scale-free networks to significantly speed up breath-first type searches (also called burning algorithms) which typically run in $O(N)$ time (Adamic et al. 2001; Kim et al. 2002). Instead of broadcasting a query to all neighbors who in turn broadcast it further, their algorithm checks whether the target is among its first neighbor, and if not, it passes the query along to the neighbor with the highest degree. This neighbor continues the search in a similar way, and if a dead end is reached, the message is recursively back-

tracked until there are no neighbors left to explore. This strategy can improve the performance to $O(N^{1/2})$ for $\gamma = 3$, and $O(\log N)$ for $\gamma = 2$ scale-free networks. The method was tested by the authors on the GNUTELLA peer-to-peer network, as well as by Kim et al. on scale-free networks generated by the configuration model and the Barabási-Albert model (Kim et al. 2002). (Kim, Yoon, Han and Jeong proposed the strategy independently a few months after Adamic et al. submitted their paper.)

Searchability of social networks has been revisited several times since Milgram's experiment. Killworth and Bernard found that the choice of neighbor to pass the letter on was most often based on common characteristics with the target, such as geographical location and profession (Killworth and Bernard 1978). An electronic version of the experiment carried out by Dodds et al. concluded that the search on the e-mail network is also guided by reliance on common "social identities", and the chosen routes do not favor social hubs (Dodds et al. 2003). Motivated by these results, Watts et al. and Kleingerg independently proposed a searchable social network model in which nodes are grouped in a nested hierarchy of social categories. A link between two nodes is exponentially less likely if their social distance (length of the path along the hierarchical tree of social groups) is large (Kleinberg 2002; Watts et al. 2002). In a simulated Milgram-type experiment, the letter would be passed from a node to a neighbor with the smallest social distance to the target. Such a search performs well for a range of the model parameters, with it's best performance scaling as $O(\log N)$ (Kleinberg 2002).

Future Directions

The short account of research advances into dynamics on complex networks presented here is by no means exhaustive. Several fairly large and lively research areas, synchronization, boolean networks, random walks on complex networks, brain networks, models of adaptive or dynamical wiring among them, have all been omitted here.

Future directions in networks research are hard to account for in a few paragraphs. It is believed that further understanding of dynamics on complex networks is the general direction of the field. Along with a shift from pure structural studies to dynamics, there has also been a shift from studies of networks in general and features that are common to most of them to more application-driven studies of increasingly narrow classes of networks. This is not to say that important lessons learned this way do not often carry over from one system to the other, but it shows that enough is known about network characteristics now to tell them apart, to look for distinguishing features as well as universal ones.

A fairly standard toolkit for the assessment of the structural properties of a network has already emerged, making the notion of networks and knowledge about them a useful toolkit in studying the architecture of complex systems. Our hope is that dynamical studies will further extend the toolkit to cover general aspects of the type of events occurring on complex networks, and perhaps lead the way in understanding how function emerges in complex systems.

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Centralities in Complex Networks

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Article Outline

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Glossary

Adjacency matrix The *adjacency matrix*, $\mathbf{A}$, of a network is a $N \times N$ matrix ($N = |V|$) with element $A_{ij} = 1$ if there is an edge from node i to node j and $A_{ij} = 0$ otherwise. If the network is weighted, $A_{ij} = w_{ij}$ where $w_{ij} \in \mathbb{R}$ is the weight associated with the edge between nodes i and j if it exists and $A_{ij} = 0$ otherwise. For undirected network, $A_{ij} = A_{ji}$ i.e., $\mathbf{A}$ is symmetric.

Connected components A *connected component* of an undirected graph $G(V, E)$ is a subgraph of G , made of a subset of V and all the edges connecting nodes of the subset together, where there exists a path between each pair of nodes. In directed graphs, we differentiate *strongly connected components*, where there exists a path in both directions between all pairs of nodes, and *weakly connected components*, where there exists a path in at least one direction between all pairs of nodes.

Degree of a node The *degree*, k_i , of node i in an undirected network is equal to its number of connections, i.e., $k_i = \sum_j A_{ij}$. For directed

network, we differentiate the *in-degree*, $k_i^{\text{in}} = \sum_j A_{ji}$ and the *out-degree*, $k_i^{\text{out}} = \sum_j A_{ij}$, i.e., the number of edges incoming to node i and outgoing from node i , respectively. In weighted undirected networks, the degree of a node is replaced by its *strength*, $s_i = \sum_j w_{ij}$ or *in-strength* and *out-strength* for weighted directed networks.

Network A *network* is a collection of nodes (also called vertices) and edges (also called links) linking pair of nodes. Mathematically, it is represented by a graph $G = (V, E)$ where V is the set of nodes and $E \subseteq V \times V$ is the set of edges. Additional information can be attached to each node or edge, for example, edges can have different weights. Edges can be undirected or directed.

Path A *path* on a graph is a walk in which all vertices and edges are distinct.

Walk A *walk* is an alternating sequence of vertices and edges in which every vertex is incident to both the edges that come before and after it in the sequence.

Why Study Networks?

In network science complex systems are represented as a mathematical graph consisting of a set of nodes representing the components and a set of edges representing their interactions. The framework of networks has led to significant advances in the understanding of the structure, formation, and function of complex systems (Albert and Barabasi 2002; Newman 2003; Boccaletti et al. 2006; Barrat et al. 2008). Social and biological processes such as the dynamics of epidemics (Pastor-Satorras et al. 2015), the diffusion of information in social media (Zhang et al. 2016), the interactions between species in ecosystems (Montoya et al. 2006), or the communication between neurons in our brains (Bullmore and Sporns 2009) are all actively studied using dynamical models on complex networks. In all of these systems, the patterns of connections at

the individual level play a fundamental role on the global dynamics and finding the most important nodes allows one to better understand and predict their behaviors.

Definition of the Subject

Real-world complex networks are characterized by a number of structural features differentiating them from regular networks, such as lattices, but also making them different than completely random graphs, such as Erdős-Rényi graphs (Newman 2003). The properties that can be found in complex networks include, for example, a modular organization, also called community structure (Fortunato 2010), or the so-called small-world effect, i.e., the fact that most pairs of nodes are connected by a very short path compared to the sizes of the networks (Watts and Strogatz 1998). A characteristic of real-world complex networks that interests us here and that has been intensively studied is the fact that their degree distributions are usually very heterogeneous (Albert and Barabasi 2002; Newman 2003), indicating that there are usually large differences in the number of connections that nodes have. Many real-world networks have been found to have degree distributions resembling power laws and are sometimes referred to as scale free (Barabási 2009). Whether these real-world systems are really scale free and whether their degree distributions are really power laws is still disputed (Holme 2019). However, what is undeniable is the fact that many real-world networks have degree distributions that are heavy tailed with a minority of the nodes concentrating the majority of the connections.

In these systems, a small set of essential nodes can shape the collective dynamics of the entire systems. For example, during epidemic outbreaks of infectious diseases, some individuals, known as *super-spreaders*, infect disproportionately more secondary contacts, as compared to most others (Kitsak et al. 2010; Stein 2011), keystone species in ecology are responsible for the integrity and stability of ecosystems (May 1972; Mills et al. 1993; Scheffer et al. 2012; Morone et al. 2019) and specific regions in brain networks are more

important than others in the formation of memory (Bullmore and Sporns 2009; Zamora-López et al. 2010; Reis et al. 2014; Del Ferraro et al. 2018). In social networks, a small set of influencers can drive the global dynamics of the system (Bovet and Makse 2019) and opinion leaders are capable of influencing the public viewpoint on certain trending topics (Watts and Dodds 2007). An important research effort in network science has therefore been dedicated to the development of methods allowing to find the most important nodes in networks. Intuitively, nodes with a large degree are likely to be more successful to trigger large-scale propagations or to control a large number of nodes. The degree centrality ranks nodes in terms of their degree and allows to identify highly connected *hubs* present in most real-world complex networks that play an essential role in controlling their dynamics and maintaining their integrity (Barabasi and Albert 1999; Albert et al. 2000; Cohen et al. 2001). While the degree centrality is arguably the simplest centrality measure, it only uses local information about each node to rank its centrality and more complex centrality measures have been developed in order to capture the collective network effects impacting the influence of a node. Most centrality measures are based on a notion of distance between nodes or on a way to traverse the network that allows to compute how “central” a node is compared to other nodes while capturing the heterogeneous structural patterns of complex networks. In the following, we describe centrality measures based on the notions of network traversal they rely on. This short entry aims at being an introduction to this extremely vast topic, with many contributions from several fields, and is by no means an exhaustive review of all the literature about network centralities (see, for example, (Freeman 1978; Borgatti 2005; Perra and Fortunato 2008; Landherr et al. 2010; Rodrigues 2019) for more exhaustive reviews).

Centrality Measures Based on Shortest Paths

Closeness centrality (Bavelas 1950; Beauchamp 1965; Sabidussi 1966; Dangalchev 2006) and betweenness centrality (Freeman 1978; Friedkin 1991) are two dual measures of centrality initially developed in social sciences to assess the

importance in terms of ease of access to others nodes (closeness) and brokering power (betweenness) of individuals in social networks. These centralities have since then been used in many other contexts. They are based on the assumption that information, or influence, propagates between two nodes in the most efficient way, i.e., by following the shortest path between them.

Considering an unweighted and undirected graph $G = (V, E)$, a walk on the graph G is an alternating sequence of vertices and edges in which every vertex is incident to both the edges that come before and after it in the sequence. A path on a graph is a walk in which all vertices and edges are distinct. A graph is said to be connected if there exists a path from any node to any other node in the graph. Considering the distance $\text{dist}(s, r)$ between two nodes s and r in a connected undirected and unweighted graph $G = (V, E)$ as the number of edges in the shortest path between them, the total distance of vertex v is defined as the sum of its distance to all other vertices

$$\text{dist}(s) = \sum_{r \in V} \text{dist}(s, r),$$

which is larger for vertices that are the farther away from other vertices. Therefore, the *closeness centrality* of a node s on a connected and undirected network is usually defined as (Bavelas 1950; Beauchamp 1965)

$$c_C(s) = \frac{1}{\sum_{r \in V} \text{dist}(s, r)} = \frac{1}{\text{dist}(s)} \quad (1)$$

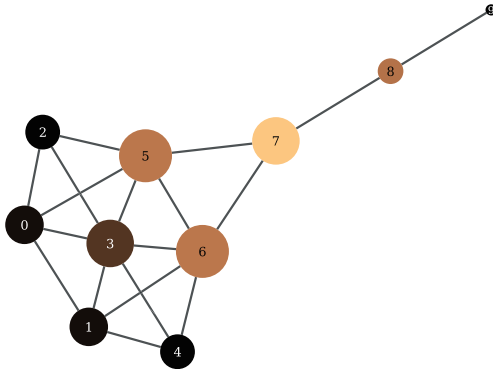
The betweenness centrality captures the brokering power of a node as the opportunity it has to intercept or influence the communications happening between pairs of other nodes. Let $\sigma(s, r)$ be the number of shortest paths between s and r and let $\sigma(s, r|b)$ be the number of shortest paths between s and r passing by a brokering node $b \in V \setminus \{s, r\}$. We consider $\sigma(s, s) = 1$ and $\sigma(s, r|b) = 0$ if $b \in \{s, r\}$. We call the quantity $\delta(s, b, r) = \frac{\sigma(s, r|b)}{\sigma(s, r)}$ the *dependency* of a sender s and a receiver r on a broker b (Brandes et al. 2016). The *betweenness centrality* in a connected and undirected graph $G = (V, E)$ is defined as the

sum of dependencies of all communicating pairs on a broker b (Freeman 1980)

$$c_B(b) = \sum_{s, r \in V} \frac{\sigma(s, r|b)}{\sigma(s, r)} = \sum_{s, r \in V} \delta(s, b, r), \quad (2)$$

and can be seen as the overall potential control of b on the communications in G . Betweenness and closeness centrality can be seen as being dual to each other conceptually expressing either the independence from the control of others (closeness) or the potential control over others (betweenness) (Freeman 1980; Brandes et al. 2016). Indeed, by noting that when considering shortest paths between s and r with different brokers b at a fixed distance d from s ($1 \leq d < \text{dist}(s, r)$) each shortest path pass through exactly one broker and therefore $\sum_{b \in V: \text{dist}(s, b) = d} \frac{\sigma(s, r|b)}{\sigma(s, r)} = 1$. This implies that the sum of dependencies between a sender s and a receiver r taken over of possible brokers b is proportional to the distance between s and r : $\sum_b \delta(s, b, r) = \sum_{d=1}^{\text{dist}(s, r)-1} \sum_{b \in V: \text{dist}(s, b) = d} \frac{\sigma(s, r|b)}{\sigma(s, r)} = \text{dist}(s, r) - 1$. This observation allows one to define the closeness centrality as $c_C(s)^{-1} = (N - 1) + \sum_{b, r \in V} \delta(s, b, r)$ revealing its mathematical duality with betweenness centrality as a different partial sum, over b and r instead of s and r , of the dependencies $\delta(s, b, r)$ showing its interpretation as a measure of lack of independence on others (Brandes et al. 2016). Figure 1 shows the kite graph introduced by Krackhardt in 1990 as an illustration of the different ranking obtained by these centrality measures (Krackhardt 1990).

In directed networks, closeness and betweenness centrality can be generalized by considering the notion of reachability instead of distance. In weighted networks where edge weights typically represent a distance or a lag in the connection between adjacent nodes, the length of a path is usually taken as being the sum of the weights of its edges. We refer the reader to (Brandes et al. 2016) for a discussion about the generalizations of the closeness and betweenness centrality to directed and weighted networks, and to their interpretations in these cases.



Centralities in Complex Networks, Fig. 1 Krackhardt kite graph showing the different ranking obtained using degree, closeness, and betweenness centralities (Krackhardt 1990). The closeness of a node is represented by its size and the betweenness of a node is indicated by its color with nodes with larger betweenness being of a lighter shade. The node with largest degree centrality is 3. Nodes 5 and 6 have the largest betweenness centrality and node 7 has the largest closeness centrality

Many variants of closeness and betweenness have been developed (Brandes 2008). The concept of betweenness centrality has also been extended to edges by considering the number of shortest paths containing an edge instead of a node in Eq. (2) (Brandes 2008) or, for example, by considering the fraction of minimum spanning trees of a graph that contain a given edge (Teixeira et al. 2015). Versions of the closeness and betweenness centralities based on random walks instead of shortest paths have also been developed (White and Smyth 2003; Newman 2005).

Centrality Measures Based on Walks

Several widely used centrality measures can be seen as being based on the concept of graph walks. Walks, alternating sequences of vertices and edges in which every vertex is incident to both the edges that come before and after it in the sequence, are useful to count the number of possible ways there is to reach a given node starting from another node. Centrality measures based on walks usually try to find the nodes from which there are the largest number of walks reaching other nodes. For unweighted networks, the number of walks of length ℓ existing between two nodes i and j is given by the element (i, j) of

the ℓ^{th} power of the adjacency matrix: $(\mathbf{A}^\ell)_{ij}$. The number of walks of length ℓ starting from node i is then given by $w(\ell)_i = \sum_j (\mathbf{A}^\ell)_{ij}$ or in matrix notation $\mathbf{w}(\ell) = \mathbf{A}^\ell \mathbf{1}$, where $\mathbf{1}$ is the unit vector. The *degree centrality* of a node i can be expressed as the number of walks of length 1 starting from it:

$$c_{\text{deg}}(i) = w(1)_i = \sum_j A_{ij}. \quad (3)$$

In order to take into account information about the surrounding of a node in its centrality score, several researchers have developed centrality measures that consider longer walks. The idea being that if a node is close to a node with a high centrality, its centrality should also be high (Katz 1953; Bonacich 1972). Starting from an initial guess for the centrality of each node given by the vector $\mathbf{x}(0)$ (e.g. $\mathbf{x}(0) = \mathbf{1}$), we can propagate this initial centrality through walks of a given length. The centrality vector for walks of length ℓ is given by

$$\mathbf{x}(\ell) = \mathbf{A}^\ell \mathbf{x}(0). \quad (4)$$

Writing the initial centrality as a linear combination of the eigenvector of the adjacency matrix, one can see that as $\ell \rightarrow \infty$ the centrality will converge to a vector proportional to the leading eigenvector of $\mathbf{A}$, the one corresponding to its largest eigenvalue, and that takes into account global information about the network structure (Newman 2010). As $\mathbf{A}$ is nonnegative and if G is connected, the Perron-Frobenius theorem ensures that the leading eigenvector is positive and that the associated eigenvalue is positive and simple. The resulting vector is called the *eigenvector centrality* whose element i is defined as

$$c_{\text{eig}}(i) \propto \sum_j A_{ij} c_{\text{eig}}(j). \quad (5)$$

In weighted networks, the eigenvector centrality is propagated along walks on the graph that are weighted by the edge weights. The eigenvector centrality can be computed similarly on directed and undirected networks with the difference that for directed networks, the adjacency matrix is in

general asymmetric and has therefore two different sets of left and right eigenvectors. Depending on the application, one may prefer to use the largest left eigenvector or the largest right eigenvector if one is more interested in nodes having a large number of incoming walks or outgoing walks, respectively. However, other types of centralities are usually preferred for directed networks as the eigenvector centrality of nodes outside of a strongly connected component (a subgraph where there exists a path in both directions between all pairs of nodes) may be equal to zero. In particular, in directed graphs without cycles (closed directed paths), the eigenvector centrality is zero for all nodes. A comparison of the degree centrality with the eigenvector centrality is shown in Fig. 2 for an undirected network of American football teams (Girvan and Newman 2002; Evans 2010).

The *subgraph centrality* is based on the idea of counting the number of times that a node takes part in the different connected subgraphs of a network, with smaller subgraphs having higher importance (Estrada and Rodríguez-Velázquez 2005). The subgraphs are identified by counting closed walks of different lengths that start and end

on a given node. The subgraph centrality of node i is defined as

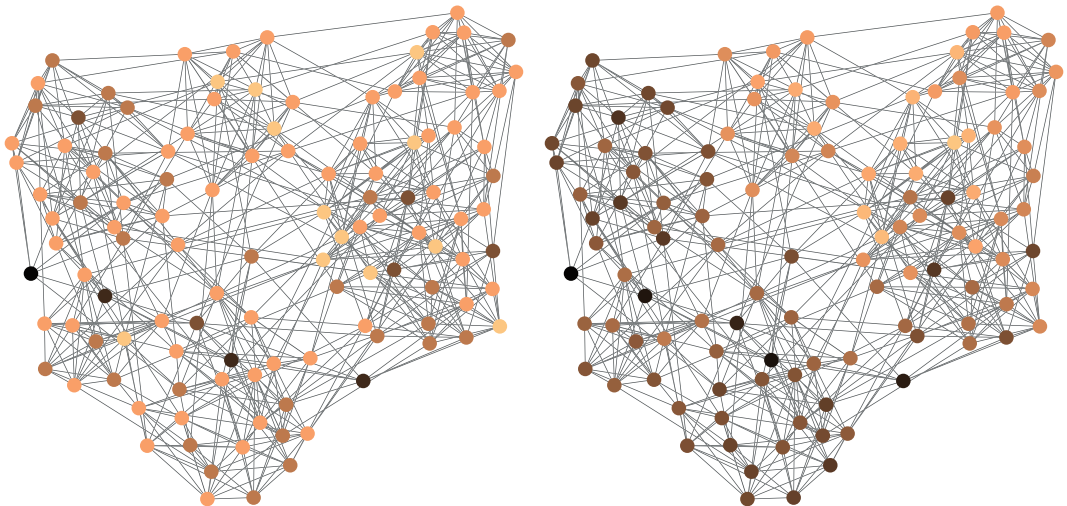
$$c_{\text{Sub}}(i) = \sum_{\ell=0}^{\infty} \frac{(\mathbf{A}^{\ell})_{ii}}{\ell!}. \quad (6)$$

By noticing that $c_{\text{Sub}}(i) = (e^{\mathbf{A}})_{ii}$, where $e^{\mathbf{A}}$ denotes the matrix exponential of $\mathbf{A}$, the subgraph centrality can be obtained from the spectrum of the adjacency matrix as (Estrada and Rodríguez-Velázquez 2005)

$$c_{\text{Sub}}(i) = \sum_{j=1}^N (v_j^i)^2 e^{\lambda_j}, \quad (7)$$

where $v_1, v_2, \dots, v_N$ form an orthonormal basis of $\mathbb{R}^N$ and are eigenvectors of $\mathbf{A}$ associated with the eigenvalues $\lambda_1, \lambda_2, \dots, \lambda_N$. This centrality is more discriminative than the degree, betweenness, closeness, or eigenvector centralities and gives a distinctly different ranking of nodes in real-world complex networks (Estrada and Rodríguez-Velázquez 2005).

Another centrality measure based on walks that tries to solve the issue of the eigenvector centrality



Centralities in Complex Networks, Fig. 2 Network of American football games between Division IA colleges during regular season Fall 2000 (Girvan and Newman 2002; Evans 2010). Degree centrality for this undirected graph is shown on the left and eigenvector centrality is shown on the right. Lighter shades indicate a higher

centrality. Several nodes have the same degree in this network making the degree centrality unable to disentangle the importance of nodes with the same degree. Eigenvector centrality has a tendency of being localized in regions where many high degree nodes are close to each other

in directed networks is the Katz centrality (Katz 1953). The Katz centrality of node i is the weighted sum of all walks emanating from i , with the count for walks of length ℓ weighted by a factor α^ℓ where $0 < \alpha < 1$. In this way the importance of longer walks is diminished compared to shorter walks. The *Katz centrality* of node i can be written as (Katz 1953)

$$c_{\text{Katz}}(i) = 1 + \sum_{\ell=1}^{\infty} \sum_j \alpha^\ell (A^\ell)_{ij}, \quad (8)$$

where the unit shift does not alter the ranking of the nodes and may be seen as arising from a single walk of length zero. In order for the centrality to converge, the factor α must be smaller than the reciprocal of the absolute value of the largest eigenvalue of $\mathbf{A}$ (Katz 1953; Bonacich 1972; Bonacich 1987). In this case, we can also note that $\mathbf{I} + \alpha\mathbf{A} + \alpha^2\mathbf{A}^2 + \alpha^3\mathbf{A}^3 + \dots = (\mathbf{I} - \alpha\mathbf{A})^{-1}$. Thus, the vector $\mathbf{x}$ giving the Katz centrality of each node is also solution of the matrix equation $\mathbf{x} = (\mathbf{I} - \alpha\mathbf{A})^{-1} \mathbf{1}$ which can be rewritten as $\mathbf{x} = \alpha\mathbf{A}\mathbf{x} + \mathbf{1}$. The Katz centrality can therefore be computed iteratively in a similar manner than the eigenvector centrality (with Eq. (4)) using

$$\mathbf{x}(t+1) = \alpha\mathbf{A}\mathbf{x}(t) + \mathbf{1}. \quad (9)$$

A unit value is added at each iteration guaranteeing that the Katz centrality will never be equal to zero, even in directed networks. The factor α can also be seen as balancing the importance of the eigenvector term compared to the constant term added at each iteration. In the limit as α approaches the reciprocal of the absolute value of the largest eigenvalue of $\mathbf{A}$, the Katz centrality approaches the eigenvector centrality on strongly connected graphs (Bonacich 1972; Bonacich 1987).

Walk-based centralities have been generalized to hypergraphs (e.g., (Bonacich et al. 2004; Benson 2019), multiplex networks (e.g., Solá et al. 2013; De Domenico et al. 2015), and temporal networks (e.g., Nicosia et al. 2013; Praprotnik and Batagelj 2015; Taylor et al. 2017).

Centrality Measures Based on Random Walks

Random walks on graphs have been extensively studied and have many applications in the study of

diffusive processes on networks and for the characterization of the structure of complex networks (Rosvall and Bergstrom 2008; Delvenne et al. 2010; Durrett 2010; Masuda et al. 2017). A random walk on a graph is defined by the trajectory of a walker that, at each time step, jumps to a neighbor of a node i with equal probability. On an unweighted and undirected network, the transition probability for a walker on node i to jump to node j is equal to

$$T_{ij} = \frac{A_{ij}}{k_i}, \quad (10)$$

or in matrix notation $\mathbf{T} = \mathbf{D}^{-1}\mathbf{A}$, where $\mathbf{D} = \text{diag}(\mathbf{k})$ is the diagonal degree matrix. In directed networks, the degree is replaced by the out-degree and in weighted networks with positive weights, the probability transition is proportional to the weight of edge (i, j) . Centrality measures based on random walks exploit the fact that, if a centrality value propagates as a random walk, at each iteration, its value is divided across all outgoing edges of a node. This is different than for eigenvector and Katz centralities, based on walks, where the centrality tends to concentrate on a few hubs in the network, leaving other nodes almost indistinguishable with very low scores due to the repeated reflection of influence along the mutual connections between hubs during iterations of Eqs. (4) and (9) (see Figs. 2 and 3).

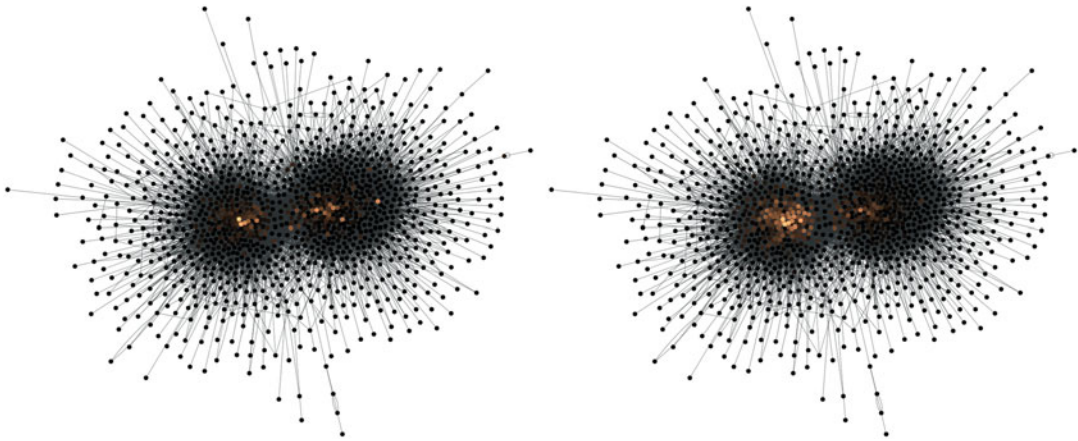
The distribution probability of finding a walker at time step n on any node of the network can be written as a row-vector $\mathbf{p}(n)$ with $\sum_i p_i = 1$. The evolution of the distribution probability is given by

$$\mathbf{p}(n+1) = \mathbf{p}(n)\mathbf{T}. \quad (11)$$

On connected undirected network, the random walk reaches a stationary distribution satisfying $\mathbf{p}^* = \mathbf{p}^*\mathbf{T}$ where the probability at each node is proportional to its degree:

$$p_i^* = \frac{k_i}{\sum_j k_j}. \quad (12)$$

On undirected networks, the degree centrality can therefore also be seen as the stationary state of



Centralities in Complex Networks, Fig. 3 A directed network of hyperlinks between weblogs on US politics, recorded in 2005 by Adamic and Glance (Adamic and Glance 2005). PageRank centrality is shown on the left

and Katz centrality is shown on the right. Lighter shades indicate a higher centrality. The Katz centrality has a tendency of being “localized” in regions with many close by hubs

the random walk process. On directed networks, random walks are not guaranteed to converge to a unique stationary state. A stationary distribution only exists on strongly connected components of a directed network (Aldous and Fill 2014; Masuda et al. 2017).

To overcome this issue the *PageRank* centrality modifies the classical random walk by introducing a “teleportation” probability, i.e., at each step the walkers have a given probability to teleport uniformly at random to any other nodes of the network. The updated equation for the PageRank probability density is given by (Brin and Page 1998; Page et al. 1999; Masuda et al. 2017)

$$\mathbf{p}(n+1) = \alpha \mathbf{p}(n) \mathbf{S} + \frac{1-\alpha}{N} \mathbf{1}^T, \quad (13)$$

where $\mathbf{S}$ is a transition matrix constructed from $\mathbf{A}$ such that $S_{ij} = A_{ij}/k_{\text{out}}(i)$ when $k_{\text{out}}(i) > 0$. For “dangling nodes,” which have no outgoing edges (i.e., $k_{\text{out}}(i) = 0$), $S_{ij} = 1/N$, meaning that a walker on such a node has a uniform probability to jump to any other nodes in the network. On non-dangling nodes, at each step, walkers have a probability $\alpha < 1$ to follow an outgoing edge and a probability $1 - \alpha$ to teleport to any node in the network. This modified random walks is now ergodic also on networks that are not strongly connected and converges to the probability

density vector giving the *PageRank* centrality of node i as

$$c_{\text{PR}}(i) = \alpha \sum_j c_{\text{PR}}(j) S_{ji} + \frac{1-\alpha}{N} \quad (14)$$

which is equal to the normalized eigenvector corresponding to the largest positive eigenvalue of the so-called Google matrix $\mathbf{G} = \alpha \mathbf{S} + \frac{1-\alpha}{N} \mathbf{1} \mathbf{1}^T$ (Ermann et al. 2015). PageRank was famously developed for ranking websites for the search engine Google considering a “random surfer model” navigating through webpages by randomly clicking on hyperlinks (Page et al. 1999). PageRank also found many applications in other aspects, such as ranking scientists and academic papers (Ding et al. 2009), images (Jing and Baluja 2008), and proteins (Ivaan and Grolmusz 2010). Figure 3 shows a comparison of the PageRank and Katz centralities on a directed network of hyperlinks between weblogs (Adamic and Glance 2005). The similarities between Eqs. (4) and (11) as well as Eqs. (9) and (13) reveal that the degree and the PageRank centralities can be seen as similar to the eigenvector and Katz centralities, but for random walks instead of regular graph walks. In the case of random walk-based centralities, one looks for eigenvectors of transition matrices instead of adjacency matrices.

Centrality Measures Based on Non-Backtracking Walks

In order to address the issue of “localization” of the eigenvector centrality mentioned above, i.e., when most of the weight of centrality vector concentrates around one or a few nodes in the network, several authors have focused on using non-backtracking walks instead of regular or random walks (Martin et al., 2014; Arrigo et al., 2018, 2020). Non-backtracking walks are graph walks where backtracking steps, i.e., steps where the walk comes back to an immediately preceding node, are not permitted. Using this type of walks can sometimes solve the problem of localization as they decrease reflections between hubs during iterations of the centrality (Martin et al., 2014). Non-backtracking walks on unweighted networks are usually described using the $2M \times 2M$ matrix $\mathbf{B}$ where rows and columns correspond to the directed edges of the network ($M = |E|$). If the network is undirected, an equivalent directed network is considered by replacing each edge by a pair of directed edges in both directions. Element $(i \rightarrow j, \ell \rightarrow h)$ of $\mathbf{B}$ is equal to one only if $j = \ell$ and $i \neq h$, i.e., there is a non-backtracking path of length 2 $i \rightarrow j \rightarrow h$ in the network. More succinctly,

$$B_{i \rightarrow j, \ell \rightarrow h} = \delta_{j\ell}(1 - \delta_{ih}), \quad (15)$$

where δ_{ij} is the Kronecker delta. The matrix $\mathbf{B}$ is referred to as the *non-backtracking matrix* or the *Hashimoto matrix* (Hashimoto 1989). Powers of $\mathbf{B}$ enumerate non-backtracking walks similarly to powers of the adjacency enumerate walks (Arrigo et al. 2020). The non-backtracking matrix is in general asymmetric with eigenvalues that are in general complex, however, since its entries are non-negatives, by the Perron-Frobenius theorem, its leading eigenvalue, λ , is real and nonnegative, and there exists a corresponding leading eigenvector, $\mathbf{v}$, whose elements are also nonnegative real numbers. If G is connected and not a tree, i.e., it has at least one cycle, λ is positive (Lin and Zhang 2019). The eigenvalues satisfy the eigenvector equation

$$\lambda \mathbf{v} = \mathbf{B} \mathbf{v} \quad (16)$$

and the *non-backtracking eigenvector centrality* of node j is defined by (Martin et al., 2014)

$$c_{\text{NBeig}}(j) = \sum_i A_{ij} v_{i \rightarrow j}. \quad (17)$$

Finding the leading eigenvector of $\mathbf{B}$ can however be computationally demanding for large graphs as the size of $\mathbf{B}$ is usually much larger than the size of $\mathbf{A}$. However, the computation can be made much faster by computing directly c_{NBeig} as the first N elements of a $2N \times 2N$ matrix called the Ihara-Bass matrix (Krzakala et al. 2013).

Non-backtracking walks have also been used to modify other centrality measures, such as the Katz (Arrigo et al., 2018), random walk (Lin and Zhang 2019), or PageRank (Aleja et al. 2019) centralities. Research on centrality measures based on non-backtracking walks is very active with recent results showing that they can also suffer from localization issues on some networks (Barucca et al. 2016; Pastor-Satorras and Castellano 2020).

Non-backtracking walks are also used in the problem of influence maximization: finding the minimal set of nodes, the *influencers*, which, if activated, would cause the spread of information to the whole network, or, if immunized, would prevent the diffusion of a large-scale epidemic (Kempe et al. 2003). Influence maximization can be mapped to the problem of optimal percolation of random networks (Morone and Makse 2015) which consist in identifying the minimal set of nodes whose removal would dismember the network in many disconnected and nonextensive components. The fragmentation of the network is measured by the size of the largest connected component, called the giant component of the network.

The intuition behind the usage of non-backtracking walks in the optimal percolation problem comes from the fact that the giant component is held together by long paths and that powers of the non-backtracking matrix allows to quickly find them. The removal of nodes is represented with the vector $\mathbf{n} = (n_1, \dots, n_N)$ where $n_i = 0$ if i is removed (influencer) or $n_i = 1$ otherwise. Considering undirected locally tree-like random graphs, a modified $2M \times 2M$ non-

backtracking matrix $\mathbf{M}$ is then defined as $M_{i \rightarrow j, \ell \rightarrow h} = n_\ell B_{i \rightarrow j, \ell \rightarrow h}$. Given an initial arbitrary positive vector $\mathbf{w}(0)$, repeated iterations with $\mathbf{M}$,

$$w(n)_{i \rightarrow j} = \sum_{kl} M_{i \rightarrow j, k \rightarrow l} w(n-1)_{k \rightarrow l}, \quad (18)$$

increase the norm of the vector as the influence of nodes on non-backtracking walks of increasingly larger lengths is included. The growth rate of the vector's norm is determined by the value of the largest eigenvalue, $\lambda(\mathbf{n})$, of the modified non-backtracking matrix. As the influencer nodes are removed, the value of $\lambda(\mathbf{n})$ decreases until the giant component is reduced to a tree (a graph without cycles) plus only one cycle when $\lambda(\mathbf{n}) = 1$. The removal of supplementary nodes quickly destroys the giant component and $\lambda(\mathbf{n})$ falls to zero (Morone and Makse 2015). The optimal influence problem can therefore be rephrased as finding the optimal configuration $\mathbf{n}$ that minimizes the largest eigenvalue of $\mathbf{M}$ (Morone and Makse 2015), which consists in removing the nodes that are on the most non-backtracking walks in the network and that are keeping the giant component connected. The *collective influence* (Morone and Makse 2015) of a node, defined as

$$CI_\ell(i) = (k_i - 1) \sum_{j \in \partial \text{Ball}(i, \ell)} (k_j - 1), \quad (19)$$

where $\partial \text{Ball}(i, \ell)$ is the set of the nodes at a distance i from ℓ , is a measure of which node to remove in order to produce the largest diminution of the largest eigenvalue of non-backtracking matrix. The ranking of the nodes in term of collective influence is produced by removing the node with the largest CI value, recomputing the CI values of its neighbors and repeating the operation until the giant component of the network disappears. An advantage of CI is that it gives a high rank to seemingly "weak nodes" with a small number of connections that are in fact surrounded by highly connected nodes and therefore on the path of many non-backtracking walks. The problem of influence maximization in networks is actively researched using many different approaches (see, for example, Braunstein et al. 2016; Mugisha and Zhou 2016;

Zdeborová et al. 2016; Radicchi and Castellano 2016; Pan et al. 2016; Pei et al. 2020).

Conclusion and Future Directions

We have seen that there is not a single measure of centrality in networks and that one should carefully choose an appropriate measure depending on the subject of investigation. In practice, centrality measures should be chosen depending on whether the network is directed or not and whether, for example, one is looking for highly connected nodes, nodes with the most brokering power, nodes that share the most influence with each others, or the minimal set of nodes that can spread information to the whole network. The differences in ranking obtained from different centrality measures should also be examined in order to better understand the signification of each ranking in a given context.

The research landscape on centrality measures for complex networks is much vaster than what has been presented in this short entry. Research is very active with recent and future directions including, for example, the properties of centrality measures based on non-backtracking walks (Pastor-Satorras and Castellano 2020), centralities in signed networks (networks where weights can be positive or negative) (Liu et al. 2020), and multilayer networks (Solá et al. 2013; De Domenico et al. 2015; Wang and Zou 2018; Wu et al. 2019). Research is also active on the development of centralities for specific applications based on network dynamics not necessarily captured by network traversals. Examples include centralities for social networks based on game theoretical concepts (Shapley 1953; Gómez et al. 2003; Michalak et al. 2013), centralities for detecting vulnerabilities in power grids based on networks of oscillators (Gutierrez et al. 2013; Tyloo et al. 2018; Tyloo et al. 2019), or centralities for identifying key genes in gene regulatory networks based on the propagation of biological signals (Zotenko et al. 2008; Missiuro et al. 2009; Kim et al. 2011; Cowen et al. 2017).

Research is also ongoing about the development of centralities in network models that extend the concept of network as an ensemble of static

pairwise relations, namely centralities in temporal networks, i.e., time-evolving networks (Nicosia et al. 2013; Praprotnik and Batagelj 2015; Taylor et al. 2017; Flores and Romance 2018; Lv et al. 2019), and in hypergraphs or simplicial complexes, i.e., generalizations of graphs where an edge can join more than two nodes (Bonacich et al. 2004; Estrada and Ross 2018; Benson 2019; Aksoy et al. 2020; Serrano and Gaomez 2020).

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Optimization Problems and Algorithms from Computer Science

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Glossary

Combinatorial optimization The search for an optimal configuration in terms of a cost function on a discrete set of allowed configurations.

Ground state The configuration of a model for a physical system of many interacting degrees of freedom described by a Hamiltonian or energy function that has the lowest energy. Also denoted as the global minimum of the energy of the system.

Disordered system A physical system with frozen in or quenched in homogeneities, usually modeled by an energy function containing parameters that are random numbers obeying in prescribed probability distribution.

Universal properties Properties that do not depend on microscopic details of a physical

system, like the critical exponents at a continuous phase transition or fractal dimensions.

Network flows A function defined on the edges of a graph that obeys mass balance constraints at each node. A number of polynomial optimization problems relevant for disordered systems can be formulated as network flow models.

Definition of the Subject

Optimization problems in statistical physics occur whenever the ground state of a classical model for a complex condensed matter system has to be determined, which is necessary for understanding its low temperature properties. In some cases calculating the ground state is an easy task as for instance for the paradigmatic model for a ferromagnet: The configuration of all magnetic moments or spins with the lowest energy is the one, where all spins point in the same direction. But usually the situation is much more complex and the problem of calculating the state with the lowest energy is highly non-trivial. This occurs typically in systems with quenched disorder and/or frustration, which means that their Hamiltonian or energy function consists of competing terms that cannot be satisfied simultaneously. Powerful algorithms from computer science have been devised to find the optimum of complex cost-functions and in some cases this can even be achieved in polynomial time. In recent years many of these algorithms could be successfully applied to physically relevant model systems: to polymers in random media, interface problems in random ferromagnets, magnetic flux-lines in disordered environments, spin glasses, and many more.

Introduction

Solid materials which contain a substantial degree of quenched disorder, so called disordered systems, have been an experimental and a theoretical challenge for physicists for many decades. The different thermodynamic phases emerging in random

magnets, the aging properties and memory effects of spin glasses, the disorder induced conductor-to-insulator transition in electronic or bosonic systems, the collective behavior of magnetic flux lines in amorphous high temperature superconductors, and the roughening transition of a disordered charge density wave systems are only a few examples for these fascinating phenomena that occur due to the presence of quenched disorder.

Analytic studies of models for these systems are usually based on perturbation theories valid for weak disorder, on phenomenological scaling pictures or on mean-field approximations. Therefore the demand for efficient numerical techniques that allow the investigation of the model Hamiltonians of disordered systems has always been high. Three facts make life difficult here: (1) The regime, where disorder effects are most clearly seen, are at low temperatures – and are even best visible at zero temperature; (2) the presence of disorder slows the dynamics of these systems down, they become *glassy*, such that for instance conventional Monte-Carlo or molecular dynamics simulations encounter enormous equilibration problems; (3) any numerical computation of disordered systems has to incorporate an extensive disorder average.

In recent years more and more model systems with quenched disorder were found that can be investigated numerically (1) at zero temperature, (2) without equilibration problems, (3) extremely fast, in polynomial time (for reviews see [1–3]). This *is* indeed progress, which became possible by the application of *exact* combinatorial optimization algorithms developed by mathematicians and computer scientists over the last few decades. This gift is not for free: first a mapping of the problem of finding the *exact* ground state of the model Hamiltonian under consideration onto a standard combinatorial optimization problem has to be found. If one is lucky, this problem falls into the class of *P*-problems, for which polynomial algorithms exist. If not, the intellectual challenge for the theoretical physicist remains to reformulate the model Hamiltonian in such a way that its universality class is not changed but a mapping on a *P*-problem becomes feasible.

An optimization problem can be described mathematically in the following way: let $\underline{\sigma} = (\sigma_1, \dots, \sigma_n)$ be a vector with n elements

which can take values from a domain $X^n : \sigma_i \in X$. The domain X can be either discrete, for instance $X = \{0, 1\}$ or $X = \mathbb{Z}$ the set of all integers (in which case it is an integer optimization problem) or X can be continuous, for instance $X = \mathbb{R}$ the real numbers. Moreover, let $\mathcal{H}$ be a real valued function, the cost function or objective, or in physics usually the Hamiltonian or the energy of the system. The *minimization problem* is then:

Find $\underline{\sigma} \in X^n$, which minimizes $\mathcal{H}$!

A maximization problem is defined in an analogous way. It is sufficient to consider only minimization problems, since maximizing a function H is equivalent to minimizing $-H$. Minimization problems in which the set X is *countable* are called *combinatorial* [4–6]. Optimization methods for real valued variables are treated mainly in mathematical literature and in books on numerical methods, see e.g. [8].

Constraints, must hold for the solution, may be expressed by additional equations or inequalities. An arbitrary value of $\underline{\sigma}$, which fulfills all constraints, is called *feasible*. Usually constraints can be expressed more conveniently without giving equations or inequalities. A famous example is the Traveling Salesman Problem (TSP) [7].

The TSP has attracted the interest of physicist several times. For an introduction, see [9]. The model is briefly presented here. Consider n cities distributed randomly in a plane. Without loss of generality the plane is considered to be the unit square. The minimization task is to find the shortest round-tour through all cities which visits each city only once. The tour stops at the city where it started. The problem is described by

$$X = \{1, 2, \dots, n\} \quad (1)$$

$$H(\underline{\sigma}) = \sum_{i=1}^n d(\sigma_i, \sigma_{i+1}) \quad (2)$$

where $d(\sigma_\alpha, \sigma_\beta)$ is the distance between cities σ_α and σ_β and $\sigma_{n+1} \equiv \sigma_1$. The constraint that every city is visited only once can be realized by constraining the vector $\underline{\sigma}$ to be a permutation of the sequence $[1, 2, \dots, n]$.

The optimum order of the cities for a TSP depends on their exact positions, i.e. on the random values of the distance matrix d . It is a feature of all problems we will encounter here that they are characterized by various random parameters. Each random realization of the parameters is called an *instance* of the problem. In general, if we have a collection of optimization problems of the same (general) type, we will call each single problem an instance of the general problem.

Because the values of the random parameters are fixed for each instance of the TSP, one speaks of *frozen* or *quenched* disorder. To obtain information about the general structure of a problem one has to average measurable quantities, like the length of the shortest tour for the TSP, over the disorder.

In this article we give an overview of *methods* how to *solve* these problems, i.e. how to find the optimum. Interestingly, there is no single way to achieve this. For some problems it is very easy while for others it is rather hard, this refers to the time you or a computer will need at least to solve the problem, it does not say anything about the elaborateness of the algorithms which are applied. Additionally, within the class of hard or within the class of easy problems, there is no universal method. Usually, even for each kind of problem there are many different ways to obtain an optimum. Once a problem becomes large, i.e. when the number of variables n is large, it is impossible to find a minimum by hand. Then computers are used to obtain a solution. Only the rapid development in the field of computer science during the last two decades has pushed forward the application of optimization methods to many problems from science and real life.

We will review some of the most fruitful applications of polynomial algorithms from the realm of combinatorial optimization to various problems in the statistical physics of disordered systems. The next section presents the application of Dijkstra's algorithm for finding shortest paths in weighted networks to the model of a non-directed polymer in a disordered environment with isotropical correlations. Then, in the fourth and fifth section, we discuss minimum cost flow problems on weighted graphs and its solution via the successive shortest path algorithm and apply it to the entanglement transition of elastic lines in a disordered environment and to the loop percolation

transition in a vortex glass model. In the sixth section we focus on the minimum cut-maximum flow problem and discuss among its many applications the roughening transition of elastic media in a disordered environment. The seventh section is devoted to the random field Ising model and how its ground states can be computed with maximum-flow-minimum-cut techniques. The spin glass problem is presented in the eighth section with a mapping onto minimum weighted matching in two dimensions and a brief outline of branch and cut methods for the higher dimensional case. The ninth section is devoted to finite temperature properties of the random bond Potts model and how its free energy can be computed in the limit of infinite Potts states. An outlook in the tenth section closes this chapter.

Polymers in a Disordered Environment

A well studied model of a single elastic line [10], like an individual polymer or a single magnetic flux line in a type-II superconductor, in a disordered environment is the following: If one excludes overhangs (and by this also self-overlaps) of the elastic lines one can parametrize its configuration by the longitudinal coordinate z . The line configuration can then be described by the transverse coordinate $\mathbf{r}(z)$ as a function of z . The presence of disorder is usually modeled by a random potential energy $V(\mathbf{r}, z)$ and the ground state configuration of the line is highly nontrivial due to the competition between the elastic energy, that tends to straighten the line, and the random energy, that tries to bend the line into positions of favorable energy:

$$\begin{aligned}\mathcal{H}_{\text{single-line}} &= \mathcal{H}_{\text{elastic}} + \mathcal{H}_{\text{random}} \\ &= \int_0^H dz \left\{ \frac{\gamma}{2} \left[\frac{d\mathbf{r}}{dz} \right]^2 + V[\mathbf{r}(z), z] \right\},\end{aligned}\tag{3}$$

where H is the longitudinal length (not the proper length) of the line. The random potential energy is a Gaussian variable with prescribed mean and correlations $\langle\langle V[\mathbf{r}, z] V[\mathbf{r}', z'] \rangle\rangle = g(\mathbf{R} - \mathbf{R}')$, where $\mathbf{R} = (\mathbf{r}, z)$ and $\langle\langle \dots \rangle\rangle$ denotes the average over the disorder.

A lattice version of this continuum model is the *directed* polymer model: The lines correspond to directed paths on a hyper-cubic lattice that start at a specific lattice site, say $(0, 0, \dots, 0)$ and proceed only in the $(1, 1, \dots, 1)$ direction along the bonds. The energy contribution for a path passing bond $\mathbf{i}$ of the lattice is a *positive* random variable e_i and the total energy of a path $\mathcal{P}$ is simply

$$\mathcal{H}_{\text{single-line}}^{\text{lattice}} = \sum_{\mathbf{i} \in \mathcal{P}} e_i = \sum_{\mathbf{i}} e_i n_i, \quad (4)$$

where $n_i = 1$ if the path passes bond $\mathbf{i}$ (i.e. $\mathbf{i} \in \mathcal{P}$) and $n_i = 0$ otherwise.

One is interested in isotropically correlated disorder and consider the problem on a *non-directed* (square) lattice (i.e. paths can pass any bond in both directions) in order not too exclude overhangs right from the beginning. In case of uncorrelated disorder overhangs were shown to be irrelevant [12], but for isotropically correlated disorder this is not clear. The latter is defined to decay algebraically with the spatial distance of the bonds

$$\langle\langle e_i - e_j \rangle\rangle = |\mathbf{R}_i - \mathbf{R}_j|^{2\alpha-1}, \quad (5)$$

where $\mathbf{R}_i$ spatial position of bond $\mathbf{i}$ and α is the correlation exponent: Note that one expects short-range correlations like $\langle\langle e_i - e_j \rangle\rangle \propto \exp(-|\mathbf{R}_i - \mathbf{R}_j|/\lambda)$ with a finite correlation length λ , to be irrelevant and only long-range correlations like (5) to change the universality class of the system. Increasing α imply stronger correlations, uncorrelated disorder corresponds to $\alpha \rightarrow -\infty$. The kind of correlated disorder described by (5) can be realized by generating correlated random numbers are generated using a well-established numerical procedure [11].

Exact ground states of the Hamiltonian (4) or optimal paths are calculated using Dijkstra's algorithm (note that all energies e_i are positive). This simple polynomial algorithm works as follows: Let $V = \{1, \dots, L^d\}$ be the set of lattice sites and $A = \{(i, j) | i, j \in V \text{ nearest neighbors}\}$ the set of bonds. The algorithm increases successively a subset S of sites for which the optimal path starting at the fixed site s are known. Obviously

initially $S = \{s\}$. We denote the energy of the optimal path starting at s and terminating at i with $E(i)$ and since all optimal paths can be constructed via a predecessor list, we keep track of this list, too, via an array $\text{pred}(i)$, denoting the predecessor site of site i in a **shortest path** from s to i :

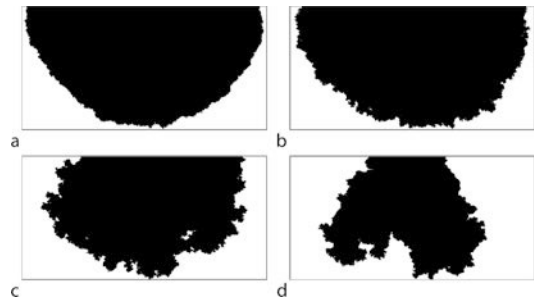
```

algorithm Dijkstra
begin
   $S := \{s\}; \bar{S} := V \setminus \{s\};$ 
   $E(s) := 0, \text{pred}(s) := 0;$ 
  while  $|S| < |V|$  do
    begin
      choose  $(i, j) : E(j) := \min_{k, m} \{E(k) + e_{(k, m)} | k \in S, m \in \bar{S}, (k, m) \in A\};$ 
       $\bar{S} := \bar{S} \setminus \{j\}; S := S \cup \{j\};$ 
       $\text{pred}(j) := i;$ 
    end
  end

```

In Fig. 1 we show examples of the set of lattice sites that are end-points of optimal paths starting from a fixed initial site and having a total energy $E(i)$ less than a given value $E_{\max}$. For uncorrelated disorder the surface of this set is roughly a semi-circle, whereas for strongly correlated disorder the surface becomes topologically more complicated.

The universal properties of the optimal paths are typically described the scaling of two characteristic quantities: The average transverse fluctuations $\langle\langle \mathbf{r}^2 \rangle\rangle$ and the average energy fluctuations



Optimization Problems and Algorithms from Computer Science, Fig. 1 Example for the growth front of the non-directed polymer for uncorrelated disorder (a and b) and correlated disorder (c and d; $\alpha = 0.4$). The black pixels indicate the lattice sites of the (square) lattice are connected via optimal paths to the offspring (center of the top line) with energy less than a given value. (From Ref. [13])

$\langle\langle E^2 \rangle\rangle$. Both are expected to grow algebraically with the longitudinal distance H between starting point and end point of the paths:

$$\begin{aligned} \langle\langle \mathbf{r}^2 \rangle\rangle &\propto H^\nu \quad \text{and} \\ \langle\langle E^2 \rangle\rangle &\propto H^\omega, \end{aligned} \quad (6)$$

where ν is called the roughness exponent and ω the energy fluctuation exponent. For uncorrelated disorder ($\alpha \rightarrow \infty$) one knows $\nu = 2/3$ and $\omega = 1/3$. By computing the optimal paths for several thousands of samples for a given disorder correlation exponent α and for a given longitudinal distances H and fitting the resulting data for transverse and energy fluctuations to the expected power laws we can extract the exponents ν and ω (for details see [13]). The resulting estimates in 2d show that the correlations are relevant for $\alpha > 0$ and the roughness exponent increases linearly for $\alpha > 0$ from its value for uncorrelated disorder $\nu = 2/3$. Although the number of overhangs in the optimal paths we computed in the non-directed case increased with α (i.e. increasing correlations) the fraction of bonds contributing to overhangs scaled to zero for all values of α we considered. Hence overhangs appear to be irrelevant also in the presence of correlated disorder.

Many Repulsive Elastic Lines in Random Media

When one puts interacting elastic lines together into a finite system with a given density of lines they will show interesting collective behavior. Examples are the entanglement of magnetic flux lines in high- T_c superconductors in the mixed phase [14] or the entanglement of polymers in materials like rubber [15]. The degree of entanglement of the lines usually manifests itself in various measurable properties like stiffness or shear modulus in the case of polymers and in transport or dynamical properties for magnetic flux lines in superconductors. A theoretical description of these line systems can be based on the single line Hamiltonian (3) plus an appropriate line interaction term:

$$\begin{aligned} \mathcal{H}_{\text{many-lines}} &= \sum_{i=1}^N \mathcal{H}_{\text{single-line}}^{(i)} \\ &+ \sum_{i < j} \int_0^L dz \int_0^L dz' V_{\text{int}}[\mathbf{R}_i(z) - \mathbf{R}_j(z')], \end{aligned} \quad (7)$$

where $\mathbf{R}_i(z) = (\mathbf{r}_i(z), z)$ is the spatial position of the infinitesimal line segment dz of the i th line. If the interactions $V_{\text{int}}[\mathbf{R}_i(z) - \mathbf{R}_j(z')]$ are short ranged (i.e. in case of flux lines the screening length small compared to the average line distance) or just hard core repulsive, and the random, δ -correlated disorder potential $V_r[\mathbf{r}_i(z), z]$ in (3) is strong compared to the elastic energy ($\propto \gamma$) this continuum model reduces to a lattice model reminiscent of the single-line lattice model (4):

$$\mathcal{H}_{\text{many-lines}}^{\text{lattice}} = \sum_{\mathbf{i}} e_{\mathbf{i}} n_{\mathbf{i}}, \quad (8)$$

where $n_{\mathbf{i}} = 1$ if a line passes bond $\mathbf{i}$ and $n_{\mathbf{i}} = 0$ otherwise and the *positive* random variable $e_{\mathbf{i}}$ is the energy cost for a line segment to occupy bond $\mathbf{i}$. The hard core constraint is thus enforced on the bonds but for the sake of an easier formal description we allow the lines to touch in isolated points, the lattice sites. The lines live on the bonds of a simple cubic lattice with a lateral width L and a longitudinal height H ($L \times L \times H$ sites) with free boundary conditions in all directions. Each line starts and ends at an arbitrary position on the bottom respective top planes. The number N of lines threading the sample is fixed by a prescribed density $\rho = N/L^2$. For a single line $N = 1$, one recovers the non-directed polymer model (4). The random bond energies are uniformly distributed over the interval $[0, 1]$.

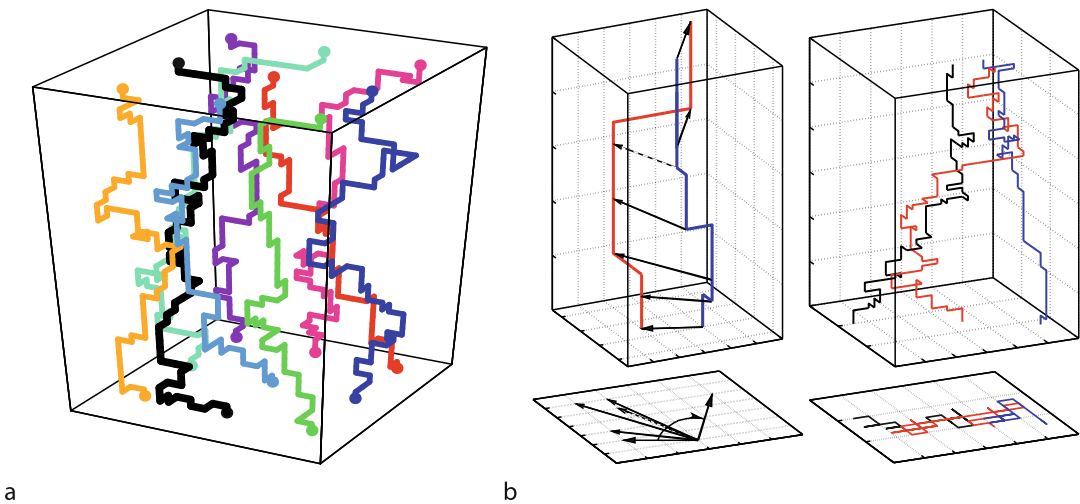
Note that the allowed configurations of the bond variables $n_{\mathbf{i}}$ are only those that can be identified with lines threading the samples (or loops inside the sample, which, however, cost energy and therefore do not occur in the ground state), which means that the number of occupied bonds connected to a lattice site that lies neither on the top nor on the bottom plane has always to be even. If we connect all sites on the top to an extra site, called the source, an all sites on the bottom to

another extra site, called the target, than the latter statement remains true also for the top and bottom plane. We can now say that N lines start at the source node and terminate at the target node, or, in network flow jargon: The feasible configurations of the variables n_i constitute a flow with zero excess on all lattice sites and an excess $+N$ and $-N$ for the source and target node, respectively.

Thus the determination of the ground state configuration of the N -line problem with the Hamiltonian (8) is a **minimum-cost-flow-problem**, which can be solved with a successive shortest path algorithm [1–3]. In essence one starts with the zero flow $n_i = 0$, corresponding to zero lines in the system, and sends successively one unit of flow from the source to the target, corresponding to adding one line after the other to the system. This has to happen with the minimal energy, i.e. along optimal paths, which are calculated using Dijkstra's algorithm that we encountered already in the single line problem discussed in the last section. However, when trying to add a line to a system with a number, say M , of lines already present, the existing line configuration sometimes must be changed to minimize the total energy for $M + 1$ line solution. That becomes feasible by allowing flow to be sent *backwards* on already occupied bonds. By this operation one

gains energy (whereas occupying an empty bond i always costs energy $e_i \geq 0$), which means one has to operate on a network that has to be adapted to the existing flow configuration and has negative energies on all occupied bonds. Unfortunately Dijkstra's algorithm works only for positive bond energies, and one has either to use a slower (label-correcting) algorithm to find the optimal paths in a graph with negative edge costs [3] or one has to use the concept of node potentials, by which one can make all energies in the adapted network non-negative without changing the actual shortest paths. This procedure is described in full detail in [3].

The resulting line configuration is then analyzed. One computes the winding angle of all line pairs as indicated in Fig. 2 (c.f. [16]). For each z -coordinate the vector connecting the two lines is projected onto that basal plane (*left part of Fig. 2*). $z = 0$ gives the reference line with respect to which the consecutive vectors for increasing z -coordinate have an angle $\phi(z)$. If the two lines intersect one neglects the intersection point and interpolate between the last and the next point in such a way that the global winding angle is minimized. One defines two lines to be *entangled* when $\phi(z) > 2\pi$. This choice is one that measures entanglement from the topological perspective [17], and comes



Optimization Problems and Algorithms from Computer Science, Fig. 2 *Left:* Ground state configuration of a N -line system with $N = 9$ defined by (8). The entry/exit points are fixed in a regular 3×3 array for better visibility. *Right:* Definition of the winding angle of two flux lines.

Right part, top: A configuration of three lines that are entangled. *Right part, bottom:* The projection of the line configuration on the basal plane, defining a connected cluster

from the requirement that an entangled pair of lines can not be separated by a suitable linear transformation in the basal plane (i.e. the lines almost always would cut each other, if one were shifted). The precise definition of entanglement is not of major relevance, and the one used is useful since it is the computationally easiest.

Sets or *bundles* of pairwise entangled lines are formed so that a line belongs to a bundle if it is entangled at least with one other line in the set. The topological multi-line-entanglement could be characterized by other measures as well; the universal properties of the transition will not depend on these. These line bundles are spaghetti-like – i.e. topologically complicated and knotted sets of one-dimensional objects. To study the size distribution of these objects one projects these bundles on the basal plane, as indicated in Fig. 2, where a bundle projects onto a connected cluster. The probability for two lines to be entangled increases with increasing system height. Consequently one would expect that the bundle size increases with H , and therefore also their projections, the clusters. This scenario is exemplified in Fig. 3, for the largest height the largest cluster spans from one side of the system to the other, i.e. it *percolates*.

Hence, for a given line density ρ one expects that for system heights larger than a critical value

H_c a system spanning large entangled bundle occurs, containing an infinite number of lines in the limit $L \rightarrow \infty$. One calls this an *entanglement transition* occurring at a finite system height H_c . In the projection plane this appears like a percolation transition and in [18] it was shown that this transition is in the same universality class as conventional bond percolation.

Vortex Glasses and Loop Percolation

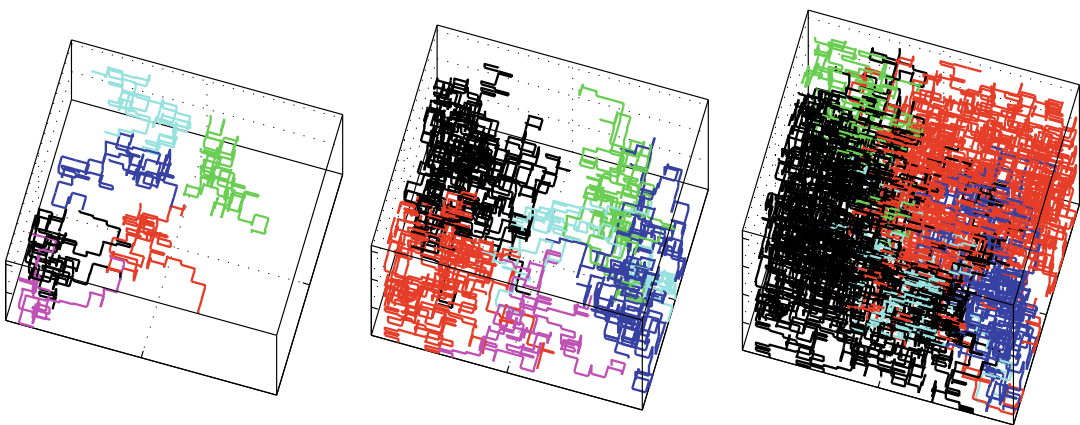
Another application of the successive shortest path algorithm for minimum-cost-flow-problems is finding the ground state of the Hamiltonian

$$H = \sum_{\mathbf{i}} (n_{\mathbf{i}} - b_{\mathbf{i}})^2$$

(9)

with the constraint $\forall k : \sum_{l \text{ n. n. of } k} n_{(kl)} = 0$,

where the integer variables $n_{\mathbf{i}}$ live on the bonds $\mathbf{i}$ of a d -dimensional hyper-cubic lattice and $b_{\mathbf{i}} \in [-2\sigma, 2\sigma]$ are real valued quenched random variables with $\sigma \geq 0$ setting the strength of the disorder. The constraint $\sum_{l \text{ n. n. of } k} n_{(kl)} = 0$ means that at all lattice sites k the incoming flow has to balance the outgoing flow, i.e. the flow $\{n_{\mathbf{i}}\}$ is divergenceless. The physical motivation of studying models these kind of models is the following:



Optimization Problems and Algorithms from Computer Science, Fig. 3 Line configurations for different heights H (from left to right: $H = 64, 96, 128$), the lateral size $L = 20$, the line density is $\rho = 0.3$. Only the largest line

bundles are shown, indicated by a varying gray scale. *Black* denotes the largest cluster, which eventually percolates

In 2d the Hamiltonian (9) occurs for instance in the context of the solid-on-solid (SOS) model on a disordered substrate [19]. The SOS representation of a 2d surface is defined by integer height variables u_k for each lattice site k of a square lattice. The disordered substrate is modeled via random offsets $d_k \in [0, 1]$ for each lattice site, such that the total height at lattice site k is $h_k = u_k + d_k$. The total energy of the surface is

$$\begin{aligned} \mathcal{H}_{\text{SOS}} &= \sum_{(kl)} (h_k - h_l)^2 \\ &= \sum_{(\bar{k}\bar{l})} \left(n_{(\bar{k}\bar{l})} - b_{(\bar{k}\bar{l})} \right)^2 \end{aligned} \quad (10)$$

where the first sum runs over all nearest neighbor pairs (kl) of the square lattice and the second sum runs over all bonds $(\bar{k}\bar{l})$ of the *dual* lattice (being a square lattice, too), which connect the centers of the elementary plaquettes of the original lattice. A dual bond $(\bar{k}\bar{l})$ therefore crosses perpendicularly a bond (kl) connecting neighbors k and l on the original lattice. We define $n_{(\bar{k}\bar{l})} = n_k - n_l$ and $d_{(\bar{k}\bar{l})} = d_l - d_k$ if l is either the right or the upper neighbor of k (i.e. for $k = (x, y)$ either $l = (x + 1, y)$ or $l = (x, y + 1)$) and $n_{(\bar{k}\bar{l})} = n_l - n_k$ and $d_{(\bar{k}\bar{l})} = d_k - d_l$ if l is either the left or the lower neighbor of k (i.e. for $k = (x, y)$ either $l = (x - 1, y)$ or $l = (x, y - 1)$). In this way the sum over all four dual bond variables attached to one site of the dual lattice corresponds to the sum of original height variables around an elementary plaquettes in the original lattice: $(n_{(x, y)} - n_{(x, y + 1)}) + (n_{(x, y + 1)} - n_{(x + 1, y + 1)}) + (n_{(x + 1, y + 1)} - n_{(x + 1, y)}) + (n_{(x + 1, y)} - n_{(x, y)}) = 0$, which implies that the flow $\{n_{(\bar{k}\bar{l})}\}$ is divergence free as inferred in (9).

In 3d the Hamiltonian (9) is the strong screening limit of the vortex glass model for disordered superconductors [20, 21].

$$\mathcal{H}_{\text{VG}} = \sum_{i,j} (n_i - b_i) G_\lambda(\mathbf{r}_i - \mathbf{r}_j) (n_j - b_j), \quad (11)$$

where the integer vortex variables n_i live on the bonds of a simple cubic lattice and have to fulfill the constraint in (9) since they represent magnetic vortex lines that are divergence free.

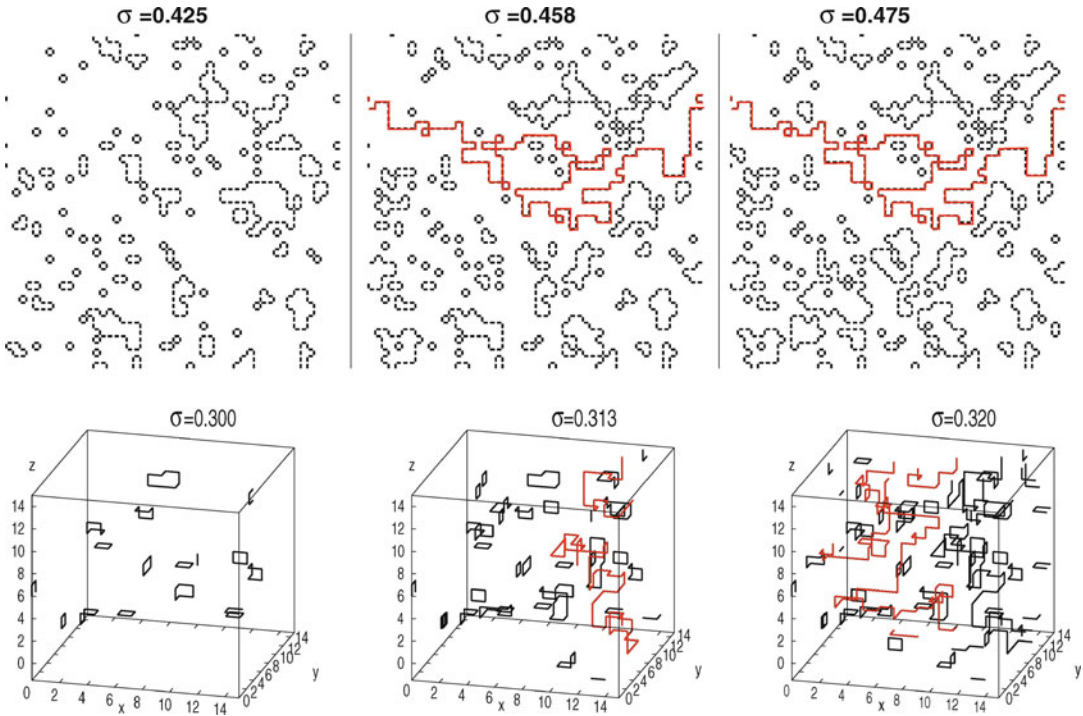
The real valued quenched random variables $b_i \in [-2\sigma, 2\sigma]$ are derived from the lattice curl of a random vector potential ($\sigma \geq 0$ being the strength of the disorder). The 3d vector $\mathbf{r}_i$ denotes the spatial positions of bond i in the lattice and the sum runs over all bond pairs of the lattice (not only nearest neighbors). The lattice propagator $G_\lambda(\mathbf{r})$ has the asymptotic form $G_\lambda(\mathbf{r}) \propto \exp(-|\mathbf{r}|/\lambda)/|\mathbf{r}|$, where λ is the screening length. In the strong screening limit $\lambda \rightarrow 0$ only the on-site repulsion survives [20] and gets.

$$\mathcal{H}_{\text{VG}}^{\lambda \rightarrow 0} = \sum_i (n_i - b_i)^2 \quad (12)$$

which is the Hamiltonian (9) in 3d that we intend to discuss here.

The ground state of (9) can again be computed within polynomial time by a successive shortest path algorithm [3]. As for the N -line problem one starts with a configuration $\{n_i\}$ that optimizes the Hamiltonian in (9) but does not, in general, fulfill the mass balance constraint given in (9). In the N -line problem that was simply the zero-flow $n_i = 0$, which does not fulfill the requirement that the source and the target have excess $+N$ and $-N$, respectively. Here we start with n_i the closest integer to the real number b_i for each bond i . Since this solution violates the mass-balance constraint one successively sends flow from nodes that have an excess flow to nodes that have a deficit along optimal paths that are again found using node potentials (to make all costs non-negative) and Dijkstra's algorithm. The details of this algorithm can be found in [1–3].

Figure 4 shows three typical ground state configurations for different strength of the disorder σ in 2d and in 3d. For small σ only small isolated loops occur, whereas for larger σ one finds loops that extend through the whole system, they percolate. A finite size scaling study of the underlying percolation transition [22] yields a novel universality class with numerically estimated critical exponents that differ significantly from those for conventional bond- or site-percolation [22].



Optimization Problems and Algorithms from Computer Science, Fig. 4 Examples of ground state configurations of the Hamiltonian (9) for varying disorder strengths σ (for particular disorder realizations). *Top*: 2d,

$L = 50$, the critical disorder strength is $\sigma_c \approx 0.46$; *Bottom*: 3d, $L = 16$, the critical disorder strength is $\sigma_c \approx 0.31$. The occupied bonds ($n_i \neq 0$) are marked *black*, the percolating loop is marked by *light gray (red)*

Interfaces and Elastic Manifolds

A system of strongly interacting (classical) particles or other objects, like magnetic flux lines in a type-II superconductor (as we discussed in Sect. “Many Repulsive Elastic Lines in Random Media” and for which the starting Hamiltonian would given by (7)), or a charge density wave system in a solid, will order at low temperatures into a regular arrangement a lattice (crystal lattice or flux line lattice). Fluctuations either induced by thermal noise (temperature) or by disorder (impurities, pinning centers) induce deviations of the individual particles from their equilibrium positions. As long as these fluctuations are not too strong an expansion of the potential energy around these equilibrium configuration might be appropriate. An expansion up to second order is called the elastic description or elastic approximation, which in a coarse grained form (where the individual particles that undergo displacements from their equilibrium positions do not occur

any more and are replaced by a continuum field $\phi(\mathbf{r})$ reads then.

$$\begin{aligned} \mathcal{H}_{\text{manifold}} &= \mathcal{H}_{\text{elastic}} + \mathcal{H}_{\text{random}} \\ &= \int d^d \mathbf{r} \left\{ \frac{\gamma}{2} |\nabla \phi(\mathbf{r})|^2 + V(\phi(\mathbf{r}), \mathbf{r}) \right\}. \end{aligned} \quad (13)$$

The random potential energy is a delta-correlated Gaussian variable with mean zero, $\langle V(\phi, \mathbf{r}) V(\phi', \mathbf{r}') \rangle = D^2 \delta(\phi - \phi') \delta(\mathbf{r} - \mathbf{r}')$. The integration extends over the whole space that parameterizes the manifold, for instance $d = 1$ for an elastic line in a random potential, $d = 2$ for an interface or a surface in a disordered environment etc. Note that for $d = 1$ one recovers the single line Hamiltonian (3). The many-line Hamiltonian (7) also allows such an elastic description in the limit, in which the interactions are strong and the random potential is weak compared to the elastic energy. In this limit the lines will only deviate moderately from a regular, translationally invariant

configuration (the Abrikosov flux line lattice). This case is called an elastic periodic medium and one has to modify the φ -part of the disorder correlator such that the Hamiltonian has the correct translational symmetry [26].

Elastic Manifold

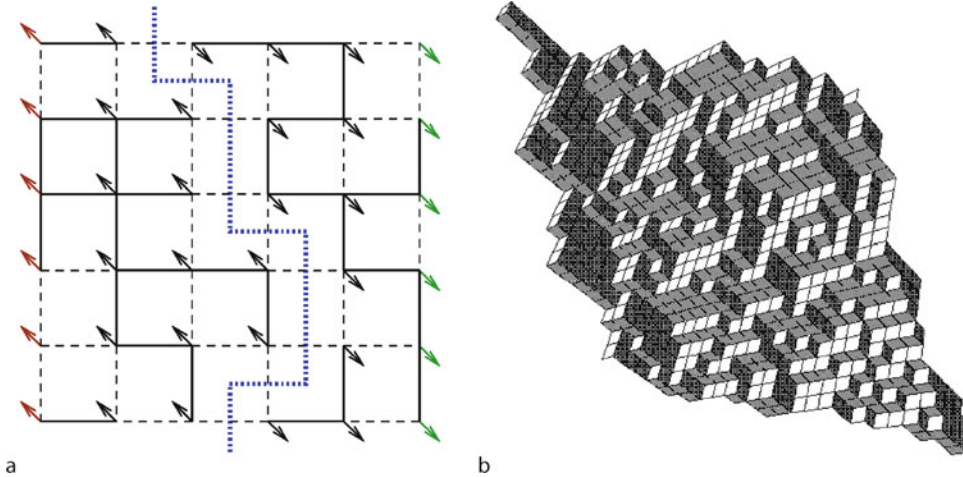
The typical example for an elastic manifold in a disordered environment are domain walls in the $d + 1$ dimensional random bond ferromagnet $H = -\sum_{\langle i,j \rangle} J_{ij} \sigma_i \sigma_j$ ($J_{ij} \geq 0$, random) in which we fix all spins in the lower (upper) plane, i.e. all σ_i with $i = (x_1, \dots, x_d, y)$ and $y = 1$ ($y = H$), to be $\sigma_i = +1$ (-1), c.f. Fig. 5. First one maps it onto a flow problem in a capacitated network. One introduces two extra sites, a source node s , which is connected to all spins of the hyperplane $y = 1$ with bonds $J_s, (x_1, \dots, x_d, y = 1) = J_\infty$, and a sink node t , which is connected to all spins of the hyperplane $y = H$ with bonds $J_s, (x_1, \dots, x_d, y = H) = J_\infty$. One chooses $J_\infty = 2 \sum_{\langle i,j \rangle} J_{ij}$, i.e. strong enough that the interface cannot pass through a bond involving one of the two extra sites. Now we enforce the aforementioned boundary conditions for the spins in the upper and the lower plane by simply fixing $\sigma_s = +1$ and $\sigma_t = -1$. The graph underlying the capacitated network one has to

consider is now defined by the set of vertices (or nodes) $N = \{1, \dots, H \cdot L^d\} \cup \{s, t\}$ and the set of edges (or arcs) connecting them $A = \{(i, j) | i, j \in N, J_{ij} > 0\}$.

The capacities u_{ij} of the arcs (i, j) is given by the bond strength J_{ij} . For any spin configuration $\mathbf{ff} = (\sigma_1, \dots, \sigma_N)$ one defines $S = \{i \in N | \sigma_i = +1\}$ and $\bar{S} = \{i \in N | \sigma_i = -1\} = N \setminus S$. Obviously $\sigma_s \in S$ and $\sigma_t \in \bar{S}$. The knowledge of S is sufficient to determine the energy of any spin configuration via $H(S) = -C + 2 \sum_{(i,j) \in (S, \bar{S})} J_{ij}$ where $(S, \bar{S}) = \{(i, j) | i \in S, j \in \bar{S}\}$. The constant $C = \sum_{(i,j) \in A} J_{ij}$ is irrelevant, i.e. independent of S . Note that $(S, \bar{S})$ is the set of edges (or arcs) connecting S with $\bar{S}$, this means it cuts N in two disjoint sets. Since $s \in S$ and $t \in \bar{S}$, this is a so called s - t -cut-set, abbreviated $[S, \bar{S}]$. Thus the problem of finding the ground state configuration of an interface in the random bond ferromagnet can be reformulated as a **minimum cut** problem

$$\min_{S \subset N} \{H'(S)\} = \min_{[S, \bar{S}]} \sum_{(i,j) \in (S, \bar{S})} J_{ij}. \quad (14)$$

in the above defined capacitated network (with $H' = (H + C)/2$). It does not come as a surprise that this minimum cut is *identical* with the



Optimization Problems and Algorithms from Computer Science, Fig. 5 Left: Sketch of a 2d (RBIM) with antiperiodic boundary conditions. Broken lines represent weak bonds, full lines strong bonds, the spin configuration with the lowest energy defines an interface, as indicated,

and corresponds to the minimum cut in the corresponding network flow problem. Right: An optimal interface in the 111-direction of a 3d RBIM corresponding to the ground state configuration of a 2d elastic medium with scalar displacement field. (From Ref. [23])

interface between the $(\sigma_i = +1)$ -domain and the $(\sigma_i = -1)$ -domain that has the lowest energy. Actually any s - t -cut-set defines such an interface, some of them might consist of many components, which is of course energetically unfavorable.

A flow in the network G is a set of nonnegative numbers x_{ij} subject to a capacity constraint and a mass balance constraint for each arc

$$\begin{aligned} 0 &\leq x_{ij} \leq u_{ij} \\ \text{and } \sum_{\{j|(i,j) \in A\}} x_{ij} - \sum_{\{j|(j,i) \in A\}} x_{ji} &= \begin{cases} -v & \text{for } i = s \\ +v & \text{for } i = t \\ 0 & \text{else} \end{cases} \end{aligned} \quad (15)$$

This means that at each node everything that goes in has to go out, too, with the only exception being the source and the sink. What actually flows from s to t is v , the value of the flow. The **maximum flow problem** for the capacitated network G is simply to find the flow $\mathbf{x}$ that has the maximum value v under the constraint (15).

Let $\mathbf{x}$ be a flow, v its value and $[S, \bar{S}]$ an s - t -cut. Then, by adding the mass balances for all nodes in S one has $v = \sum_{(i,j) \in (S, \bar{S})} x_{ij} - \sum_{(i,j) \in (\bar{S}, S)} x_{ji}$ and since $x_{ij} \leq u_{ij}$ and $x_{ji} \geq 0$ the following inequality holds: $v \leq \sum_{(i,j) \in (S, \bar{S})} u_{ij} = u[S, \bar{S}]$. Thus the value of any flow $\mathbf{x}$ is less or equal to the capacity of any cut in the network. If one discovers a flow $\mathbf{x}$ whose value equals to the capacity of some cut $[S, \bar{S}]$, then $\mathbf{x}$ is a maximum flow and the cut is a minimum cut. The following implementation of the augmenting path algorithm constructs a flow whose value is equal to the capacity of a s - t -cut it defines simultaneously. Thus it will solve the maximum flow problem (and, of course, the minimum cut problem).

Given a flow $\mathbf{x}$, the residual capacity r_{ij} of any arc $(i, j) \in A$ is the maximum additional flow that can be sent from node i to node j using the arcs (i, j) and (j, i) . The residual capacity has two components: (1) $u_{ij} - x_{ij}$, the unused capacity of arc (i, j) , (2) x_{ji} the current flow on arc (j, i) , which one can cancel to increase the flow from node i to j $r_{ij} =$

$u_{ij} - x_{ij} + x_{ji}$. The residual network $G(\mathbf{x})$ with respect to the flow $\mathbf{x}$ consists of the arcs with *positive* residual capacities. An augmenting path is a directed path from the node s to the node t in the residual network. The *capacity of an augmenting path* is the minimum residual capacity of any arc in this path.

Obviously, whenever there is an augmenting path in the residual network $G(\mathbf{x})$ the flow $\mathbf{x}$ is not optimal. This motivates the following generic augmenting path algorithm:

algorithm Ford-Fulkerson

begin

Initially set $x_{ij} := 0$, $x_{ji} := 0$ for all $(i, j) \in A$;

do

construct residual network R with capacities r_{ij} ;

if there is an augmenting path from s to t in G **then**

begin

Let $r_{\min}$ the minimum capacity of r along this path;

Increase the flow in N along the path

by a value of $r_{\min}$;

end

until no such path from s to t in G is found;

end

This algorithm is polynomial in the number of lattice sites if the distribution of capacities is discrete (binary for instance). In the general case it has to be improved and there are indeed more efficient algorithms to solve this problem in polynomial time. One of them is the push/relabel algorithm introduced by Goldberg and Tarjan [24]. It determines the maximal flow by successively improving a “preflow”. A preflow is an edge function $f(e)$ that obeys the range constraint $0 \leq f(e) \leq w(e)$, but the conservation constraint at each node is relaxed: the sum of the $f(e)$ into or out of a node can be nonzero at internal (physical) nodes. The amount of violation of conservation at each node v give “excesses” $e(v)$. The basic operations of the algorithm, push and relabel, are used to rearrange these excesses. When the preflow can no longer be improved, it can, if desired, be converted to a maximal flow, proving the correctness of the algorithm. For details see [24, 25]. It

can be applied in the way sketched above to compute universal geometrical properties of elastic manifolds in 2 and 3 dimensions [23].

Periodic Medium

The presence of a periodic background potential, like a crystal potential, has a smoothening effect on the elastic manifold and tends to lock it into one of its minima. The competition between the random potential, that roughens the manifold, and such a periodic potential might lead to a roughening transition [27, 28]. In 2d this is actually not the case [29], but in 3d there is as we will see. We consider a lattice version of the Hamiltonian

$$\mathcal{H} = \mathcal{H}_{\text{manifold}} + H_{\text{periodic}} \quad (16)$$

$$\text{with } H_{\text{periodic}} = \int d^d \mathbf{r} V_{\text{periodic}}(\phi(\mathbf{r})),$$

where $V_{\text{periodic}}(\phi) = -\cos \phi$ represents the periodic potential.

We introduce a discrete solid-on-solid (SOS) type interface model for the elastic manifold whose continuum Hamiltonian is given in Eq. (16). Locally the EM remains flat in one of periodic potential minima at $\phi = 2\pi h$ with integer h . Due to fluctuations, some regions might shift to a different minimum with another value of h to create a step (or domain wall) separating domains. To minimize the cost of the elastic and periodic potential energy in Eq. (16), the domain-wall width must be finite, say ξ_o . Therefore, if one neglects fluctuations in length scales less than ξ_o , the continuous displacement field $\phi(\mathbf{r})$ can be replaced by the integer height variable $\{h_{\mathbf{x}}\}$ representing a $(3+1)d$ SOS interface on a simple cubic lattice with sites $\mathbf{x} \in \{1, \dots, L\}^3$. The lattice constant is of order ξ_o and set to unity. The energy of the interface is given by the Hamiltonian

$$\mathcal{H} = \sum_{\langle \mathbf{x}, \mathbf{y} \rangle} J_{(h_{\mathbf{x}}, \mathbf{x}); (h_{\mathbf{y}}, \mathbf{y})} |h_{\mathbf{x}} - h_{\mathbf{y}}| - \sum_{\mathbf{x}} V_R(h_{\mathbf{x}}, \mathbf{x}), \quad (17)$$

where the first sum is over nearest neighbor site pairs. After the coarse graining, the step energy

$J > 0$ as well as the random pinning potential energy V_R becomes a quenched random variable distributed independently and randomly. Note a periodic elastic medium has the same Hamiltonian as in Eq. (17) with random but periodic J and V_R in h with periodicity p [30]. In this sense, the elastic manifold emerges as in the limit $p \rightarrow \infty$ of the periodic elastic medium.

To find the ground state, one maps the 3D SOS model onto a ferromagnetic random bond Ising model in $(3+1)d$ hyper-cubic lattice with anti-periodic boundary conditions in the extra dimension [23] (for the 3 space direction one uses periodic boundary conditions instead). The anti-periodic boundary conditions force a domain wall into the ground state configuration of the $(3+1)d$ ferromagnet. Note that bubbles are *not* present in the ground state. A domain wall may contain an overhang which is unphysical in the interface interpretation. Fortunately, one can forbid overhangs in the Ising model representation using a technique described in [23]. If the longitudinal and transversal bond strengths are assigned with $J/2$ and $V_R/2$ occurring in Eq. (17), respectively, this domain wall of the ferromagnet becomes equivalent to the ground state configuration of (17) for the interface with the same energy. The domain wall with the lowest energy is then determined exactly by using again the maxflow/min-cost algorithm.

In elastic media described by (17) the tendency of the periodic potential to lock the displacements competes with the roughening effect of the disorder. Analytically a roughening transition was predicted in [28] and the critical exponents could be numerically estimated in three dimensions [30] with the mapping and algorithm described above.

Random Field Ising Model

The random field Ising model (RFIM, for a review see [31, 32]) is defined

$$H = - \sum_{\langle ij \rangle} J_{ij} \sigma_i \sigma_j - \sum_i h_i \sigma_i \quad (18)$$

with $\sigma_i = \pm 1$ Ising spins, ferromagnetic bonds $J_{ij} \geq 0$ (random or uniform), (ij) nearest neighbor

pairs on a d -dimensional lattice and at each site i a random field $h_i \in R$ that can be positive and negative. The first term prefers a ferromagnetic order, which means it tries to align all spins. The random field, however, tends to align the spins with the field which points in random directions depending on whether it is positive or negative. This is the source of competition in this model.

Let us suppose for the moment uniform interactions $J_{ij} = J$ and a symmetric distribution of the random fields with mean zero and variance h_r . It is established by now that in 3d (and higher dimensions) the RFIM shows ferromagnetic long range order at low temperatures, provided h_r is small enough. In 1d and 2d there is no ordered phase at any finite temperature. Thus in 3d one has a paramagnetic/ferromagnetic phase transition along a line $h_c(T)$ in the h_r - T -diagram.

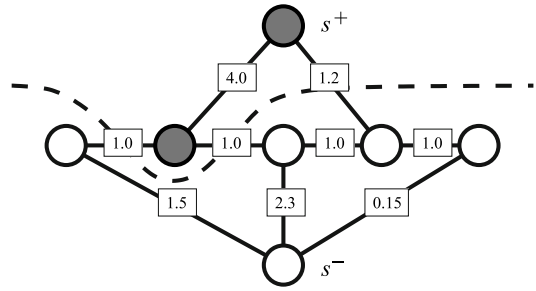
The renormalization group picture says that the nature of the transition is the same all along the line $h_c(T)$, with the exception being the pure fixed point at $h_r = 0$ and $T_c \sim 4.51 J$. The RG flow is dominated by a zero temperature fixed point at $h_c(T = 0)$. As a consequence, the critical exponents determining the critical behavior of the RFIM should be all identical along the phase transition line, in particular identical to those one obtains at zero temperature by varying h_r alone. Thus to study the universal properties of the phase transition in the RFIM one needs to calculate its ground state.

This optimization task is again equivalent to a maximum flow problem [33, 34], as in the interface model discussed in the last section. Historically the RFIM was the first physical model that has been investigated with a maximum flow algorithm [36]. However, here the minimum-cut is not a geometric object within the original system.

To map the ground state problem for the RFIM onto a max-flow-min-cut problem one proceeds in the same way as in the interface problem: One adds to extra nodes s and t and attaches spins with fixed values there (see Fig. 6):

$$\sigma_s = +1 \quad \text{and} \quad \sigma_t = -1 \quad (19)$$

One connects all sites with positive random field to the node s and all sites with negative random field to t :



Optimization Problems and Algorithms from Computer Science, Fig. 6 Representation of the ground state problem for the RFIM as an RBIM domain wall or minimum-cut problem. The physical spins are the five nodes in the single row in the figure, while the fixed external spins are s^+ and s^- . The physical RFIM coupling $J = 1.0$. A spin with $h_i > 0$ ($h_i < 0$) is connected by an auxiliary coupling of strength $h_i(-h_i)$ to s^+ (s^-). The weights of each bond are indicated: the random fields are, from left to right, $h = -1.5, +4.0, -2.3, +1.2$, and 0.15 . In the ground state, the interfacial energy between up-spin and down-spin domains is minimized, i.e., the spins are partitioned into two sets with minimal total cost for the bonds connecting the two sets. The *dashed* curve indicates the minimal weight cut. The *white* (*dark*) nodes indicate up (down) spins in the ground state configuration

$$J_{si} = \begin{cases} h_i & \text{if } h_i \geq 0 \\ 0 & \text{if } h_i < 0 \end{cases} \quad (20)$$

$$J_{it} = \begin{cases} |h_i| & \text{if } h_i < 0 \\ 0 & \text{if } h_i \geq 0 \end{cases}$$

The a network is constructed with the set of nodes $N = \{1, \dots, L^d\} \cup \{s, t\}$ and the set of (forward and backward) arcs $A = \{(i, j) | i, j \in N, J_{ij} > 0\}$. Each of them has a capacity $u_{ij} = J_{ij}$. The energy or cost function can be written as.

$$E = - \sum_{(i,j) \in A} J_{ij} \sigma_i \sigma_j \quad (21)$$

or, by denoting the set $S = \{i \in N | \sigma_i = +1\}$ and $\bar{S} = N \setminus S$

$$E(S) = -C + 2 \sum_{(i,j) \in (S, \bar{S})} J_{ij} \quad (22)$$

with $C = \sum_{(i,j) \in A} J_{ij}$. The problem is reduced to the problem of finding a minimum s - t -cut as in (14). The difference to the interface problem is that now the extra bonds connecting the two special

nodes s and t with the original lattice do not have infinite capacity: they can lie *in* the cut, namely whenever it is more favorable not to break a ferromagnetic bond but to disalign a spin with its local random field. In the extended graph the s - t -cut again forms connected interface, however, in the original lattice (without the bonds leading to and from the extra nodes) the resulting structure is generally *disconnected*, a multicomponent interface. Each single component surrounds a connected region in the original lattice containing spins, which all point in the same direction. In other words, they form ferromagnetically ordered domains separated by domain walls given by the subset of the s - t -cut that lies in the original lattice.

In passing we note that diluted Ising antiferromagnets in a homogeneous external field (DAFF) map straightforwardly onto a RFIM if the underlying lattice is bipartite. The 3d DAFF on a simple cubic lattice is defined by

$$H = + \sum_{(ij)} J_{ij} \varepsilon_i \varepsilon_j \sigma_i \sigma_j - \sum_i h_i \varepsilon_i \sigma_i \quad (23)$$

where $\sigma_i = \pm 1$, $J_{ij} \geq 0$, (ij) are nearest neighbor pairs on a simple cubic lattice, and $\varepsilon_i \in \{0, 1\}$ with $\varepsilon_i = 1$ with probability c , representing the concentration of spins. Because of the plus sign in front of the first term in (23) all interactions are antiferromagnetic, the model represents a diluted antiferromagnet, for which many experimental realizations exist (e.g. $\text{Fe}_c \text{Zn}_{1-c}\text{F}_2$). Now that neighboring spins tend to point in opposite directions due to their antiferromagnetic interaction a uniform field competes with this ordering tendency by trying to align them all. On a bipartite lattice in zero external field the ground state would be antiferromagnetic, which means that one can define two bipartite sublattices A and B . One defines new spin and field variables via

$$\sigma'_i = \begin{cases} +\sigma_i & \text{for } i \in A \\ -\sigma_i & \text{for } i \in B \end{cases}$$

$$h'_i = \begin{cases} +\varepsilon_i h_i & \text{for } i \in A \\ -\varepsilon_i h_i & \text{for } i \in B. \end{cases}$$

Since $\sigma'_i \sigma'_j = -\sigma_i \sigma_j$ for all nearest neighbor pairs (ij) one can write (23) as

$$H = - \sum_{(ij)} J'_{ij} \sigma'_i \sigma'_j - \sum_i h'_i \sigma'_i \quad (24)$$

with $J'_{ij} = J_{ij} \varepsilon_i \varepsilon_j$. This is again a RFIM and ground states can be computed with the max-flow technique.

The main focus of the application of the max-flow-min-cut algorithm to the RFIM is the phase transition in the three-dimensional model occurring at a critical disorder strength h_c at zero temperature, which separates a paramagnetic phase for large disorder strength from a ferromagnetic phase. The maximum flow algorithm has first been used by Ogielski [36] to calculate the critical exponents of the RFIM via the finite size scaling. More accurate estimates were obtained more recently by Middleton and Fisher [35], where also an detailed discussion of the problems and conflicting results about the RFIM universality class is provided. For Gaussian random fields (with variance h^2) they find for the finite size scaling of magnetization $m = [S_i]_{\text{av.}}$ and specific heat $c = N^{-1} dE/dT$ and

$$\begin{aligned} m &\sim L^{-\beta/\nu}, \\ c &\sim L^{x/\nu}, \end{aligned} \quad (25)$$

with the magnetization exponent $x = \beta/\nu = 0.012 \pm 0.004$ the correlation length exponent $\nu = 1.37 \pm 0.09$, and the specific heat exponent $\alpha = -0.07 \pm 0.17$. Note that the magnetization exponent is very close to zero, which means that the transition is hard to discriminate from a first order transition. Also the specific heat exponents is close to zero and slightly negative, implying a lack of divergence of the specific heat at the transition.

The Spin Glass Problem

Spin glasses are the prototypes of (disordered) frustrated systems (see [37]). In the models discussed up to now, the frustration was caused by two separate terms of different physical origin (interactions and external fields or boundary conditions). Spin glasses are magnetic systems in which the magnetic moments interact ferro- or anti-ferromagnetically in a random way, as in the

following Edwards–Anderson Hamiltonian for a short ranged Ising spin glass (SG)

$$H = - \sum_{(ij)} J_{ij} \sigma_i \sigma_j, \quad (26)$$

where $\sigma_i = \pm 1$, (ij) are nearest neighbor interactions on a d -dimensional lattice and the interaction strengths $J_{ij} \in \mathbb{R}$ are unrestricted in sign. In analogy to Eq. (14) one shows that the problem of finding the ground state is again equivalent to finding a minimal cut $[S, \bar{S}]$ in a network

$$\min_{\underline{\mathbf{f}}} \{H'(\underline{\mathbf{f}})\} = \min_{[S, \bar{S}]} \sum_{(i,j) \in (S, \bar{S})} J_{ij}, \quad (27)$$

again $H' = (H + C)/2$ with $C = \sum_{(i,j)} J_{ij}$. However, now the capacities $u_{ij} = J_{ij}$ of the underlying network are *not* non-negative any more, therefore it is *not* a minimum-cut problem and thus it is also not equivalent to a maximum flow problem, which we know how to handle efficiently.

It turns out that the spin glass problem is *much* harder than the questions we have discussed so far. In general (i.e. in any dimension larger than two and also for 2d in the presence of an external field) the problem of finding the SG ground state is $\mathcal{NP}$ -complete [42], which means in essence that no polynomial algorithm for it is known (and also that chances to find one in the future are marginal). Nevertheless, some extremely efficient algorithms for it have been developed [38, 39], which have a non-polynomial bound for their worst case running-time but which terminate (i.e. find the optimal solution) after a reasonable computing time for pretty respectable system sizes.

Two Dimensions, Planar Graph

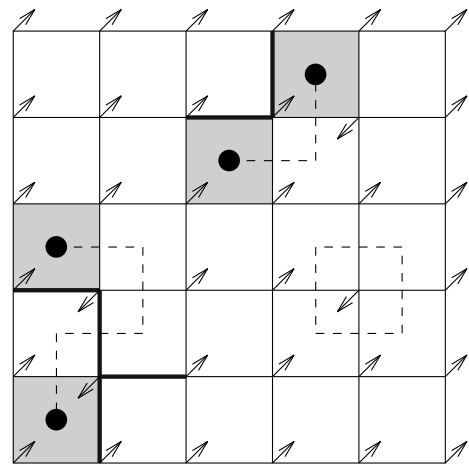
First we discuss the only non-trivial case that can be solved with a polynomial algorithm: the two-dimensional Ising SG on a planar graph. This problem can be shown to be equivalent to finding a minimum weight perfect matching, which can be solved in polynomial time. We do not treat matching problems and the algorithms to solve them in this lecture (see [4, 40, 41]), however, we would like to present the idea [42]. To be concrete let us consider a square lattice with free

boundary conditions. Given a spin configuration $\underline{\mathbf{f}}$ (which is equivalent to $-\underline{\mathbf{f}}$) we say that an edge (or arc) (i, j) is satisfied if $J_{ij} \sigma_i \sigma_j > 0$ and it is *unsatisfied* if $J_{ij} \sigma_i \sigma_j < 0$. Furthermore we say a plaquette (i.e. a unit cell of the square lattice) is *frustrated* if it is surrounded by an odd number of negative bonds (i.e. $J_{ij} \cdot J_{jk} \cdot J_{kl} \cdot J_{li} < 0$ with i, j, k and l the four corners of the plaquette). There is a one-to-one correspondence between equivalent spin configurations ($\underline{\mathbf{f}}$ and $-\underline{\mathbf{f}}$) and sets of unsatisfied edges with the property that on each frustrated (unfrustrated) plaquette there is an odd (even) number of unsatisfied edges. See Fig. 7 for illustration.

Note that

$$H(\underline{\mathbf{f}}) = -C + 2 \sum_{\text{unsatisfied edges}} |J_{ij}|. \quad (28)$$

which means that one has to minimize the sum over the weights of unsatisfied edges. A set of unsatisfied edges will be constituted by a set of paths (in the dual lattice) from one frustrated plaquette to another and a set of closed circles (see Fig. 7). Obviously the latter always increase the energy so that we can neglect them. The problem of finding the ground state is therefore



Optimization Problems and Algorithms from Computer Science, Fig. 7 Two-dimensional Ising spin glass with $\pm J$ couplings: Thin lines are positive interactions, thick lines are negative interactions, $\nearrow$ means $\sigma_i = +1$, $\searrow$ means $\sigma_i = -1$, shaded faces are frustrated plaquettes, broken lines cross unsatisfied edges

equivalent to finding the minimum possible sum of the weights of these paths between the frustrated plaquettes. This means that we have to *match* the black dots in the Fig. 7 with one another in an optimal way. One can map this problem on a minimum weight **perfect matching** problem (a perfect matching of a graph $G = (N, A)$ is a set $M \subseteq A$ such that each node has only has only one edge of M adjacent to it). This can be solved in polynomial time (see [42] for further details).

Note that for binary couplings, i.e. $J_{ij} = \pm J$, where $J_{ij} = +J$ with probability p the weight of a matching is simply proportional to the sum of the lengths of the various paths connecting the centers of the frustrated plaquettes, which simplifies the actual implementation of the algorithm. In [43] the 2d $\pm J$ spin glass and the site disordered SG has been studied extensively with this algorithm. The site disordered spin glass is defined as follows: occupy the sites of a square lattice randomly with A (with concentration c) and B (with concentration $1 - c$) atoms. Now define the interactions J_{ij} between neighboring atoms: $J_{ij} = -J$ if on both sites are A -atoms and J_{ij} otherwise.

The main application of this algorithm is directed towards studying domain walls in spin glasses since they provide informations on the low temperature behavior and the stability of the ground state with respect to thermal fluctuations. Domain walls can be induced by applying two different boundary conditions to the system (usually periodic and anti-periodic), their energy is simply the difference between the energies of the ground states with the two different boundary conditions. The domain wall energy of the two-dimensional spin glass model with Gaussian couplings scales like

$$\Delta E \sim L^\theta, \quad (29)$$

where the stiffness exponent is $\theta = -0.282$ (see [44] for a survey). The negativity of this exponent indicates the absence of stable spin glass phase at any non-vanishing temperature in the 2d spin glass model. Recently also the fractal properties of the domain walls in 2d spin glasses with Gaussian couplings became important: They have a fractal dimension of $d_f = 1.27(1)$ and it was argued [45] that they might be a realization of a

stochastic Loewner evolution (see [46] for a review) realized in disordered systems.

Three Dimensions, Non-planar Graphs

As we mentioned, in any other case except the planar lattice situation discussed above the spin glass problem is $\mathcal{NP}$ -hard. In what follows we would like to sketch the idea of an efficient but non-polynomial algorithm [39]. To avoid confusion with the minimum cut problem we discussed in connection with maximum flows one calls the problem (27) a max-cut problem (since finding the minimum of H is equivalent to finding the maximum of $-H$).

Let us consider the vector space R^A . For each cut $[S, \bar{S}]$ define $\chi^{(S, \bar{S})} \in R^A$, the incidence vector of the cut, by $\chi_e^{(S, \bar{S})} = 1$ for each edge $e = (i, j) \in (S, \bar{S})$ and $\chi_e^{(S, \bar{S})} = 0$ otherwise. Thus there is a one-to-one correspondence between cuts in G and their $\{0, 1\}$ -incidence vectors in R^A . The *cut-polytope* $P_C(G)$ of G is the convex hull of all incidence vectors of cuts in G : $P_C(G) = \text{conv}\{\chi^{(S, \bar{S})} \in R^A \mid S \subseteq A\}$. Then the max-cut problem can be written as a *linear program*

$$\max \{\underline{u}^T \underline{x} \mid \underline{x} \in P_C(G)\} \quad (30)$$

since the vertices of $P_C(G)$ are cuts of G and vice versa. Linear programs usually consist of a linear cost function $\underline{u}^T \underline{x}$ that has to be maximized under the constraint of various inequalities defining a polytope in R^n (i.e. the convex hull of finite subsets of R^n) and can be solved for example by the simplex method, which proceeds from corner to corner of that polytope to find the maximum (see e.g. [40, 41, 48]). The crucial problem in the present case is that it is $\mathcal{NP}$ -hard to write down all inequalities that represent the cut polytope $P_C(G)$.

It turns out that also *partial* systems are useful, and this is the essential idea for an efficient algorithm to solve the general spin glass problem as well as the traveling salesman problem or other so called mixed integer problems (i.e. linear programs where some of the variables x are only allowed to take on some integer values, like 0 and 1 in our case) [7, 47]. One chooses a system of linear inequalities L whose solution set $P(L)$

contains $P_C(G)$ and for which $P_C(G) = \text{convex hull}\{\mathbf{x} \in P(L) | x \text{ integer}\}$. In the present case these are $0 \leq x \leq 1$, which is trivial, and the so called cycle inequalities, which are based on the observation that all cycles in G have to intersect a cut an even number of times. The most remarkable feature of this set L of inequalities is the following:

The separation problem for a set of inequalities L consists in either proving that a vector x satisfies all inequalities of this class or to find an inequality that is violated by $\mathbf{x}$. A linear program can be solved in polynomial time if and only if the separation problem is solvable in polynomial time [49]. The separation problem for the cycle inequalities can be solved in polynomial time by the *cutting plane algorithm* which, starting from some small initial set of inequalities, generates iteratively new inequalities until the optimal solution for the actual subset of inequalities is feasible. Note that one does not solve this linear program by the simplex method since the cycle inequalities are still too numerous for this to work efficiently.

Due to the insufficient knowledge of the inequalities that are necessary to describe $P_C(G)$ completely, one may end up with a non-integral solution $\mathbf{x}^*$. In this case one *branches* on some fractional variable x_e (i.e. a variable with $x_e^* \notin \{0, 1\}$), creating two subproblems in one of which x_e is set to 0 and in the other x_e is set to 1. Then one applies the cutting plane algorithm recursively for both subproblems, which is the origin of the name *branch-and-cut*. Note that in principle this algorithm is not restricted to any dimension, boundary conditions, or to the fieldless case. However, there are realizations of it that run fast (e.g. in 2d) and others that run slow (e.g. in 3d) and it is ongoing research to improve on the latter, for an overview over the current status see [47].

Potts Free Energy and Submodular Functions

The problem addressed in this chapter is not a low temperature problem but concerns the computation of the free energy of a Potts model (see [50] for a review) at *any temperature*, including some phase transition temperatures. To transform the problem of computing the free energy into an optimization

problem (i.e. find a minimum in a finite set), one needs to take some limit. Usually this is a zero temperature limit as it was for all applications discussed so far in this article. Here this will be the limit of an *infinite number of states*.

Consider the q -state Potts model on a d -dimensional hyper-cubic lattice with periodic boundary conditions defined by the Hamiltonian:

$$H = - \sum_{\langle ij \rangle} J_{ij} \delta(\sigma_i, \sigma_j), \quad (31)$$

where σ_i are q -state Potts variables ($\sigma_i \in \{1, \dots, q\}$) located at lattice sites i , the sum goes over all nearest neighbor pairs $\langle ij \rangle$ of the lattice, and $J_{ij} > 0$ are ferromagnetic couplings (not that $\delta(\sigma, \sigma')$ is the Kronecker-delta, which means $\delta(\sigma, \sigma') = 1$ for $\sigma = \sigma'$ and $\delta(\sigma, \sigma') = 0$ for $\sigma \neq \sigma'$). The case $q = 2$ corresponds to the Ising model. In the random bond Potts model, which is of interest here, the couplings J_{ij} are random variables. In $d \leq 2$ dimensions the Potts model has phase transition at some critical temperature T from a paramagnetic to a ferromagnetic phase. Thermodynamic properties of the q -state Potts model are computed via its partition function

$$Z = \{\underline{\sigma}\} \sum \exp \left(\sum_{ij} -\beta J_{ij} \delta(\sigma_i, \sigma_j) \right). \quad (32)$$

The first sum runs over all possible spin configuration, i.e. it involves q^N terms, where N is the number of spins in the system and $\beta = 1/T$ is the inverse temperature.

In the so-called random cluster representation [51] the partition sum can be written as a sum over all subsets $U \subseteq E$ of the set of edges (or bonds)

$$\begin{aligned} Z &= \sum_{\{\sigma\}} \prod_{ij} \exp(-\beta J_{ij} \delta(\sigma_i, \sigma_j)) \\ &= \sum_{\{\sigma\}} \prod_{ij} (1 + v_{ij} \delta(\sigma_i, \sigma_j)) \end{aligned}$$

where $v_{ij} = \exp(\beta K_{ij}) - 1$. Note that the Kronecker-delta can only take on the values zero and one by which it is possible to identify $\exp(J\delta) = 1 + \delta(\exp(J) - 1) = 1 + v\delta$. Again one can

regard the lattice as a graph $G = (V, E)$, where the sites and the bonds of the lattice are the vertices V and the edges E of the graph. Then a careful bookkeeping of the terms in the development of the above expression leads to:

$$Z = \sum_{G' \subseteq G} q^{c(G')} \prod_{e \in G'} v_e, \quad (33)$$

where G' denotes any subgraph of G , i.e. a graph, possibly not connected (but all vertices are kept), where some edges of G have been deleted (there are 2^m subgraphs where m is the number of edges of G). $c(G')$ is the number of connected components of the subgraph G' . For example for the empty subgraph $G' = \emptyset$ the number of connected components is the number of sites, while for $G' = G$ it is one. The product in (33) is over all the edges in G' with the convention that the product over an empty set is one. If the parameter β is small (i.e. high temperature) then the parameters v_{ij} are small and, summing in (33), only the subgraphs with few edges provides an approximation to the partition function: this is a high temperature development. Note also the way the parameter q appears in (33): it can be extended to non integer values, relating the Potts model to other problems (percolation, etc. ...) [57].

Following [52] one can map the computation of the partition function Z of any ferromagnetic Potts model in the limit $q \rightarrow \infty$ onto an optimization problem by introducing another parametrization of the couplings with new variables w_e defined by

$$v_e = q^{w_e}.$$

Inserting this expression in (33) one gets $Z = \sum_{G' \subseteq G} q^{c(G') + \sum_{e \in G'} w_e}$, and defining $f(G) = c(G) + \sum_{e \in G} w_e$.

$$Z = \sum_{G' \subseteq G} q^{f(G')}.$$

In the limit $q \rightarrow \infty$ only the subgraphs G^* maximizing $f(G)$ will contribute, and computing the partition function of the Potts model in the infinite

number of states limit amounts to finding the subgraphs G' of the graph G maximizing the function f , i.e. minimizing the function [52]:

$$f_P(G') = - \left(c(G') + \sum_{e \in G'} w_e \right). \quad (34)$$

It turns out that this function has a property which allows to minimize it very efficiently: it is a *sub-modular function*.

Submodular Functions

The concept of a submodular function in discrete optimization appears to be in several respects analogous to that of a convex function in continuous optimization. In many combinatorial theorems and problems, submodularity is involved, in one form or another, and submodularity often plays an essential role in a proof or an algorithm. Moreover, analogous to the fast methods for convex function minimization, it turns out that submodular functions can also be minimized fast, i.e. in polynomial time.

Submodularity is a special property of *set functions*, which are defined as follows: Let V be a finite set and $2^V = \{X | X \subseteq V\}$ be the set of all the subsets of V . A function $f: 2^V \rightarrow \mathbb{R}$ is called a set function.

Now a set function f is **submodular** if for all subsets $A \subseteq V$ and $B \subseteq V$:

$$f(A) + f(B) \geq f(A \cap B) + f(A \cup B). \quad (35)$$

It is simple to show that a function f is submodular if and only if for any subsets $S \subseteq R \subseteq V$ and for any $x \in V$:

$$f(S \cup \{x\}) - f(S) \geq f(R \cup \{x\}) - f(R). \quad (36)$$

This means intuitively that adding an element to a “small” ensemble S (since $S \subseteq R$) has more effect than adding to a “large” ensemble R .

The function (34) $f_P(A) = -(c(A) + w(A))$ is sub-modular, because the function $-c(A)$ is sub-modular (and the function $w(A)$ is modular: Take two sets of edges $A \subseteq B$ and an edge e . Inspecting the three possible cases: $e \in A$, $e \notin A$ and $e \in B$,

$c(B)$, which is the reverse of (36), so that the function $-c$ is a submodular function. Note that $c(E')$ with $E' \subseteq E$ counts the number of connected components of the graph G' that contains *all* vertices V of the complete graph but only the edges in E' . Thus adding an edge will never increase the number of components.

On the other hand it is straightforward to see that the function $w(G) = \sum_{e \in G} w_e$ verifies $w(A \cup C) + w(A \cap C) = w(A) + w(C)$. It is a so-called *modular* function. Consequently the function (34) f_P is a submodular function. In summary we are looking for the sets of edges minimizing the submodular function f_P for which a *strongly polynomial* algorithm has been recently discovered.

In passing we note that we encountered other examples of submodular functions already in the preceding sections, namely the function that defines the costs of cuts in a graph with positive edge weights, which occurs the interface problem and the random field Ising model in the last sections: Take a graph $G = (V, E)$ and define C to be a function of the subsets of the V and $C(U \subseteq V)$ is the number of edges having exactly one end in U . This function can be generalized to the case where the edges are directed and weighted, i.e. each edge carries an arrow and a positive number. The function $C(U \subseteq V)$ is then the sum of the weight of the edges having the beginning vertex in U and the ending vertex not in U . This kind of function is generally called a “cut” and is submodular.

Minimization of Submodular Function

The minimization of any submodular function can be done in polynomial time. This was first published in reference [53] in 1981. In this paper the authors utilize the so-called ellipsoid method. However this method is not a combinatorial one and is far from being efficient. In that respect this result was not quite satisfactory at least for the practical applications. Eighteen years later, Iwata–Fleischer–Fujishige [54], and independently Schrijver [55] discovered a combinatorial method which is fully satisfactory from the theoretical, as well as from the practical, point of view.

The general method uses a mathematical programming formulation. The problem is

algebraically expressed as a linear program, i.e. a set of variables y_S associated to each subset $S \subset V$ is introduced, these variables are subjected to constraints and a linear function F of these variables is to be minimized. The constraints include a set of linear equations and the condition that each of the y_S is zero or one. This last condition is in general extremely difficult to realize. However, it turns out that a theorem due to Edmonds [56] indicates this condition can be simply dropped, and that automatically the set of values y_S which minimize F will all be zero or one! Actually only one variable $y_{S^*} = 1$ will be non zero and it is precisely associated to the optimal set. Combined with the dual version of this linear program, it provides a characterization of the optimal set.

The general algorithm mentioned above can be applied to minimize (34), however, due to the specific form of the function to minimize, a more suitable method does exist. For this a property that is true for any submodular function is useful. To emphasize that the function f to minimize is defined on all the subsets of a set E we will label f with the index E as f_E . Let us now consider a subset $F \subseteq E$; one can define a set function on F by $f_F(A) = f_E(A)$ for any $A \subseteq F$. If the function f_E is submodular then its restriction f_F is also submodular. We have the following property:

Let $F \subseteq E$ and $e \in E$, if A_F is an optimal set of the set function f_F defined on F , then there will be an optimal set $A_{F \cup \{e\}}$ of the function $f_{F \cup \{e\}}$ defined on $F \cup \{e\}$ such that $A_F \subseteq A_{F \cup \{e\}}$.

To make the notation simpler we denote the function $f_{F \cup \{e\}}$ on $F \cup \{e\}$ by f_1 . Let A be an optimal set of f_F on F and B an optimal set of f_1 on $F \cup \{e\}$. One has

$$f_1(A \cup B) \leq f_1(A) + f_1(B) - f_1(A \cap B) \quad (37)$$

since f_1 is submodular. But $f_1(A) = f_F(A)$ and $f_1(A \cap B) = f_F(A \cap B)$ since both A and $A \cap B$ are in A . Since A is an optimal set one has $f_F(A) \leq f_F(A \cap B)$ and consequently $f_1(A) - f_1(A \cap B) \leq 0$. Inserting this last inequality into (37) one finds that $f_1(A \cup B) \leq f_1(B)$ which proves that $A \cup B$ is one of the optimal sets (Q.E.D.).

This property has an important consequence. Indeed let us suppose that the optimal set has been found for a subset F of E . Then all the elements of E which have been selected as belonging to the optimal set of F will still belong to one optimal set of all the sets $G \supseteq F$. In other words, let us find the optimal set for $\{e_0, e_1\}$ where e_0 and e_1 are *arbitrary* elements of E ; then if we find that any of these two elements belongs to the optimal set, it will belong to one optimal set for $F \subseteq E$! Such an algorithm which makes a definitive choice at each step is called a *greedy* algorithm.

Based on this observation an efficient algorithm for the minimization of (34) was developed in [58], see also [59].

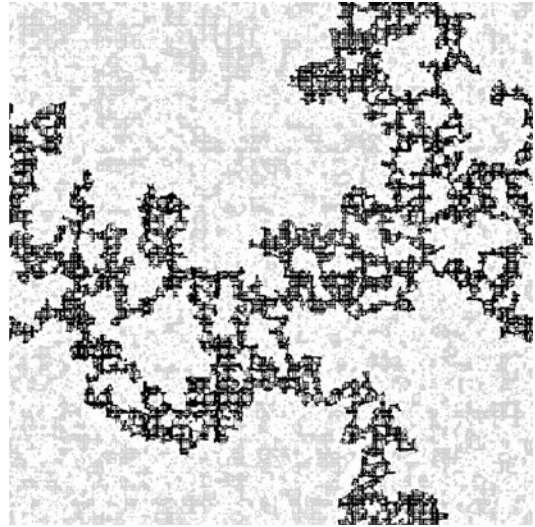
Results

The algorithm based on the ideas mentioned before and presented in detail in [58, 59], was applied to various two dimensional and three dimensional lattices. A realization of the disorder is chosen accordingly to a probability distribution. In practice all the weights $w(e)$ on the edge e are rational numbers with a common integer denominator q . In other words, we choose an integer $p(e)$ for each edge and set $w(e) = p(e)/q$. To work only with integers one maximizes the product qf :

$$qf(A) = qC(A) + \sum_{e \in A} p(e).$$

It is clear that if q is small compare to all the $p(e)$, then all the weights $w(e)$ will be large and the optimal set will be the set of all edges. On the contrary if q is large all the weights will be small and the optimal set will be empty. These two situations are easy to handle. Between this two limits the optimal set grows, and for a precise value q_c of q , which depends on the lattice, the optimal set percolates. This value corresponds to a phase transition. Depending on the lattice under consideration and on the distribution of the random variables $p(e)$ this transition can be first or second order.

In Fig. 8, one optimal set is shown for a lattice where each edge carries a weight $1/6$ or $5/6$ with probability one half (i.e. it is a critical point). The edges from the optimal set belonging to the percolation cluster are shown in black, while the



Optimization Problems and Algorithms from Computer Science, Fig. 8 A 512×512 lattice. The edges of the optimal set belonging to the percolating cluster are shown in *black*, and the edges of the optimal set not belonging to the optimal set are in *gray*. (From Ref. [59])

others are shown in gray. The percolation cluster, which is the largest connected component in the optimal subgraph $G' \subseteq G$ is fractal with a fractal dimension $d_f = 1.809$ that is related to the critical exponent $x = \beta/\nu$ for the magnetization of the random bond $q \rightarrow \infty$ Potts model (31) in two dimensions via $x = 2 - d_f = 0.191$. Surprisingly this agrees within the error bars with the magnetization exponent $x = (3 - \sqrt{5})/4$ of the random transverse Ising chain [61], which is a one-dimensional quantum spin model. A discussion of this observation and details of the computations can be found in [60].

Future Directions

We have reviewed several applications of polynomial optimization algorithms from computer science to disordered systems in statistical physics. They were used extensively in the recent years to compute numerically universal properties like critical exponents, domain wall exponents and geometrical features like roughness and stiffness with much higher precision than with Monte-Carlo methods, which suffer notoriously from

equilibration problems. A number of important issues, which were controversially debated within different analytical could be clarified, numerically, in this way – as for instance the nature of the low temperature phase of the superrough phase in the two-dimensional Bragg glass [19, 62], the absence of a stable glass phase in the strongly screened vortex glass model [21] and the issue of many states in various two-dimensional glassy models [63]. Other questions still remain to be answered, as for example the phenomenon of an apparent non-universality in the three-dimensional random field Ising model [64].

NP-hard problems occurring in the statistical physics of disordered systems, still remain a challenge: Examples are the computation of ground states of spin glass models on non-planar graphs, like the three-dimensional spin glass or the random field Potts model for three or more Potts states [65]. Stochastic optimization techniques like hysteretic optimization [66] or extremal optimization [67] have reached a high level of sophistication but naturally suffer from the lack of a proof of optimality of the resulting solution. Progress in the development of exact and efficient algorithm that can handle sufficiently large system sizes to perform a reliable finite size scaling analysis is being made [47] and highly rewarding.

The cross-fertilization between computer science and statistical physics is also fruitful in the other direction: Phase transitions that occur in some combinatorial optimization problems like the satisfiability problem (SAT) were studied intensively in recent years by physicists and remarkable progress has been achieved in understanding it and inventing efficient algorithms. These developments were not covered in this article, excellent introductions can be found in [68].

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Statistical Mechanics Approach to Econophysics

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Glossary

Probability density $P(x)$ is defined so that the probability of finding a random variable x in the interval from x to $x + dx$ is equal to $P(x) dx$.

Cumulative probability $C(x)$ is defined as the integral $C(x) = \int_x^\infty P(x) dx$. It gives the probability that the random variable exceeds a given value x .

The Boltzmann-Gibbs distribution gives the probability of finding a physical system in a state with the energy ε . Its probability density is given by the exponential function (1).

The Gamma distribution has the probability density given by a product of an exponential function and a power-law function, as in (9).

The Pareto distribution has the probability density $P(x) \propto 1/x^{1+\alpha}$ and the cumulative

probability $C(x) \propto 1/x^\alpha$ given by a power law. These expressions apply only for high enough values of x and do not apply for $x \rightarrow 0$.

The Lorenz curve was introduced by American economist Max Lorenz to describe income and wealth inequality. It is defined in terms of two coordinates $x(r)$ and $y(r)$ given by (19). The horizontal coordinate $x(r)$ is the fraction of the population with income below r , and the vertical coordinate $y(r)$ is the fraction of income this population accounts for. As r changes from 0 to ∞ , x and y change from 0 to 1, parametrically defining a curve in the (x, y) -plane.

The Gini coefficient G was introduced by the Italian statistician Corrado Gini as a measure of inequality in a society. It is defined as the area between the Lorenz curve and the straight diagonal line, divided by the area of the triangle beneath the diagonal line. For perfect equality (everybody has the same income or wealth) $G = 0$, and for total inequality (one person has all income or wealth, and the rest have nothing) $G = 1$.

The Fokker-Planck equation is the partial differential Eq. (22) that describes evolution in time t of the probability density $P(r, t)$ of a random variable r experiencing small random changes Δr during short time intervals Δt . It is also known in mathematical literature as the Kolmogorov forward equation. The diffusion equation is an example of the Fokker-Planck equation.

Definition of the Subject

Econophysics is an interdisciplinary research field applying methods of statistical physics to problems in economics and finance. The term “econophysics” was first introduced by the prominent theoretical physicist Eugene Stanley in 1995 at the conference *Dynamics of Complex Systems*, which was held in Calcutta (now known as Kolkata) as a satellite meeting to the

STATPHYS-19 conference in China (Chakrabarti 2005; Carbone et al. 2007). The term appeared in print for the first time in the paper by Stanley et al. (1996) in the proceedings of the Calcutta conference. The paper presented a manifesto of the new field, arguing that “behavior of large numbers of humans (as measured, e. g., by economic indices) might conform to analogs of the scaling laws that have proved useful in describing systems composed of large numbers of inanimate objects” (Stanley et al. 1996). Soon the first econophysics conferences were organized: *International Workshop on Econophysics*, Budapest, 1997, and *International Workshop on Econophysics and Statistical Finance*, Palermo, 1998 (Carbone et al. 2007), and the book *An Introduction to Econophysics* (Mantegna and Stanley 1999) was published.

The term “econophysics” was introduced by analogy with similar terms, such as “astrophysics,” “geophysics,” and “biophysics,” which describe applications of physics to different fields. Particularly important is the parallel with biophysics, which studies living creatures, which still obey the laws of physics. It should be emphasized that econophysics does not literally apply the laws of physics, such as Newton’s laws or quantum mechanics, to humans, but rather uses mathematical methods developed in statistical physics to study statistical properties of complex economic systems consisting of a large number of humans. So, it may be considered as a branch of applied theory of probabilities. However, statistical physics is distinctly different from mathematical statistics in its focus, methods, and results.

Originating from physics as a quantitative science, econophysics emphasizes quantitative analysis of large amounts of economic and financial data, which became increasingly available with the massive introduction of computers and the Internet. Econophysics distances itself from the verbose, narrative, and ideological style of political economy and is closer to **econometrics** in its focus. Studying mathematical models of a large number of interacting economic agents, econophysics has much common ground with the **agent-based modeling and simulation**. Correspondingly, it distances itself from the representative-agent approach of traditional

economics, which, by definition, ignores statistical and heterogeneous aspects of the economy.

Two major directions in econophysics are applications to finance and economics. Observational aspects are covered in the entry “Econophysics, Observational.” This entry, “Econophysics, Statistical Mechanics Approach to,” concentrates primarily on statistical distributions of money, wealth, and income among interacting economic agents.

Another direction related to econophysics has been advocated by the theoretical physicist Serge Galam since the early 1980s under the name “**sociophysics**” (Galam 2004), with the first appearance of the term in print in Galam et al. (1982). It echoes the term *physique sociale* proposed in the nineteenth century by Auguste Comte, the founder of sociology. Unlike econophysics, the term “sociophysics” did not catch on when first introduced, but it is coming back with the popularity of econophysics and active promotion by some physicists (Stauffer 2004; Schweitzer 2003; Weidlich 2000). While the principles of both fields have a lot in common, econophysics focuses on the narrower subject of economic behavior of humans, where more quantitative data are available, whereas sociophysics studies a broader range of social issues. The boundary between econophysics and sociophysics is not sharp, and the two fields enjoy a good rapport (Chakrabarti et al. 2006). A more detailed description of the historical development is presented in section “**Historical Introduction**.”

Historical Introduction

Statistical mechanics was developed in the second half of the nineteenth century by James Clerk Maxwell, Ludwig Boltzmann, and Josiah Willard Gibbs. These physicists believed in the existence of atoms and developed mathematical methods for describing their statistical properties, such as the probability distribution of velocities of molecules in a gas (the Maxwell-Boltzmann distribution) and the general probability distribution of states with different energies (the Boltzmann-Gibbs distribution). There are interesting connections between the development of statistical

physics and statistics of social phenomena, which were recently brought up by the science journalist Philip Ball (Ball 2002, 2004).

Collection and study of “social numbers,” such as the rates of death, birth, and marriage, has been growing progressively since the seventeenth century (see Chap. 3 in Ball 2004). The term “statistics” was introduced in the eighteenth century to denote these studies dealing with the civil “states,” and its practitioners were called “statists.” Popularization of social statistics in the nineteenth century is particularly accredited to the Belgian astronomer Adolphe Quetelet. Before the 1850s, statistics was considered an empirical arm of political economy, but then it started to transform into a general method of quantitative analysis suitable for all disciplines. It stimulated physicists to develop statistical mechanics in the second half of the nineteenth century.

Rudolf Clausius started development of the kinetic theory of gases, but it was James Clerk Maxwell who made a decisive step of deriving the probability distribution of velocities of molecules in a gas. Historical studies show (see Chap. 3 in Ball 2004) that, in developing statistical mechanics, Maxwell was strongly influenced and encouraged by the widespread popularity of social statistics at the time. This approach was further developed by Ludwig Boltzmann, who was very explicit about its origins (see p. 69 in Ball 2004):

The molecules are like individuals, and the properties of gases only remain unaltered, because the number of these molecules, which on the average have a given state, is constant.

In his book *Populäre Schriften* from 1905 (Boltzmann 1905), Boltzmann praises Josiah Willard Gibbs for systematic development of statistical mechanics. Then, Boltzmann says (cited from Austrian Central Library for Physics (2006)):

This opens a broad perspective if we do not only think of mechanical objects. Let’s consider to apply this method to the statistics of living beings, society, sociology and so forth.

(The author is grateful to Michael E. Fisher for bringing this quote to his attention.)

It is worth noting that many now-famous economists were originally educated in physics and

engineering. Vilfredo Pareto earned a degree in mathematical sciences and a doctorate in engineering. Working as a civil engineer, he collected statistics demonstrating that distributions of income and wealth in a society follow a power law (Pareto 1897). He later became a professor of economics at Lausanne, where he replaced Léon Walras, also an engineer by education. The influential American economist Irving Fisher was a student of Gibbs. However, most of the mathematical apparatus transferred to economics from physics was that of Newtonian mechanics and classical thermodynamics (Mirowski 1989). It culminated in the neoclassical concept of mechanistic equilibrium where the “forces” of supply and demand balance each other. The more general concept of statistical equilibrium largely eluded mainstream economics.

With time, both physics and economics became more formal and rigid in their specializations, and the social origin of statistical physics was forgotten. The situation is well summarized by Philip Ball (see p. 69 in Ball (2004)):

Today physicists regard the application of statistical mechanics to social phenomena as a new and risky venture. Few, it seems, recall how the process originated the other way around, in the days when physical science and social science were the twin siblings of a mechanistic philosophy and when it was not in the least disreputable to invoke the habits of people to explain the habits of inanimate particles.

Some physicists and economists attempted to connect the two disciplines during the twentieth century. The theoretical physicist Ettore Majorana argued in favor of applying the laws of statistical physics to social phenomena in a paper published after his mysterious disappearance (Majorana 1942). The statistical physicist Elliott Montroll co-authored the book *Introduction to Quantitative Aspects of Social Phenomena* (Montroll and Badger 1974). Several economists applied statistical physics to economic problems (Föllmer 1974; Blume 1993; Foley 1994; Durlauf 1997). An early attempt to bring together the leading theoretical physicists and economists at the Santa Fe Institute was not entirely successful (Anderson et al. 1988). However, by the late 1990s, the attempts to apply statistical physics to

social phenomena finally coalesced into the robust movements of econophysics and sociophysics, as described in section “[Definition of the Subject.](#)”

The current standing of econophysics within the physics and economics communities is mixed. Although an entry on econophysics has appeared in the *New Palgrave Dictionary of Economics* (Rosser 2008), it is fair to say that econophysics is not accepted yet by mainstream economics. Nevertheless, a number of open-minded, non-traditional economists have joined this movement, and the number is growing. Under these circumstances, econophysicists have most of their papers published in physics journals. The journal *Physica A: Statistical Mechanics and Its Applications* emerged as the leader in econophysics publications and has even attracted submissions from some bona fide economists. The mainstream physics community is generally sympathetic to econophysics, although it is not uncommon for econophysics papers to be rejected by *Physical Review Letters* on the grounds that “it is not physics.” There are regular conferences on econophysics, such as *Applications of Physics in Financial Analysis* (sponsored by the European Physical Society), *Nikkei Econophysics Symposium*, and *Econophysics Colloquium*. Econophysics sessions are included in the annual meetings of physical societies and statistical physics conferences. The overlap with economics is the strongest in the field of agent-based simulation. Not surprisingly, the conference series WEHIA/ESHIA, which deals with heterogeneous interacting agents, regularly includes sessions on econophysics.

Statistical Mechanics of Money Distribution

When modern econophysics started in the middle of the 1990s, its attention was primarily focused on analysis of financial markets. However, three influential papers (Drăgulescu and Yakovenko 2000; Chakraborti and Chakraborti 2000; Bouchaud and Mézard 2000), dealing with the subject of money and wealth distributions, were published in 2000. They started a new direction that is closer to economics than finance and

created an expanding wave of follow-up publications. We start reviewing this subject with Drăgulescu and Yakovenko (2000), whose results are the most closely related to the traditional statistical mechanics in physics.

The Boltzmann-Gibbs Distribution of Energy

The fundamental law of equilibrium statistical mechanics is the Boltzmann-Gibbs distribution. It states that the probability $P(\varepsilon)$ of finding a physical system or subsystem in a state with the energy ε is given by the exponential function

$$P(\varepsilon) = ce^{\frac{-\varepsilon}{T}}, \quad (1)$$

where T is the temperature, and c is a normalizing constant (Wannier 1987). Here we set the Boltzmann constant k_B to unity by choosing the energy units for measuring the physical temperature T . Then, the expectation value of any physical variable x can be obtained as

$$\langle x \rangle = \frac{\sum_k x_k e^{\frac{-\varepsilon_k}{T}}}{\sum_k e^{\frac{-\varepsilon_k}{T}}}, \quad (2)$$

where the sum is taken over all states of the system. Temperature is equal to the average energy per particle: $T \sim \langle \varepsilon \rangle$, up to a numerical coefficient of the order of 1.

Equation (1) can be derived in different ways (Wannier 1987). All derivations involve the two main ingredients: statistical character of the system and conservation of energy ε . One of the shortest derivations can be summarized as follows. Let us divide the system into two (generally unequal) parts. Then, the total energy is the sum of the parts, $\varepsilon = \varepsilon_1 + \varepsilon_2$, whereas the probability is the product of probabilities, $P(\varepsilon) = P(\varepsilon_1)P(\varepsilon_2)$. The only solution of these two equations is the exponential function (1).

A more sophisticated derivation, proposed by Boltzmann himself, uses the concept of entropy. Let us consider N particles with total energy E . Let us divide the energy axis into small intervals (bins) of width $\Delta\varepsilon$ and count the number of particles N_k having energies from ε_k to $\varepsilon_k + \Delta\varepsilon$. The

ratio $N_k/N = P_k$ gives the probability for a particle having the energy ε_k . Let us now calculate the multiplicity W , which is the number of permutations of the particles between different energy bins such that the occupation numbers of the bins do not change. This quantity is given by the combinatorial formula in terms of the factorials

$$W = \frac{N!}{N_1!N_2!N_3!\dots}. \quad (3)$$

The logarithm of multiplicity of called the entropy $S = \ln W$. In the limit of large numbers, the entropy per particle can be written in the following form using the Stirling approximation for the factorials:

$$\frac{S}{N} = -\sum_k \frac{N_k}{N} \ln \left(\frac{N_k}{N} \right) = -\sum_k P_k \ln P_k. \quad (4)$$

Now we would like to find what distribution of particles between different energy states has the highest entropy, that is, the highest multiplicity, provided that the total energy of the system, $E = \sum_k N_k \varepsilon_k$, has a fixed value. Solution of this problem can be easily obtained using the method of Lagrange multipliers (Wannier 1987), and the answer gives the exponential distribution (1).

The same result can be derived from the **ergodic theory**, which says that the many-body system occupies all possible states of a given total energy with equal probabilities. Then it is straightforward to show (Lopez-Ruiz et al. 2007a, b) that the probability distribution of the energy of an individual particle is given by (1).

Conservation of Money

The derivations outlined in section “[The Boltzmann-Gibbs Distribution of Energy](#)” are very general and use only the statistical character of the system and the conservation of energy. So, one may expect that the exponential Boltzmann-Gibbs distribution (1) may apply to other statistical systems with a conserved quantity.

The economy is a big statistical system with millions of participating agents, so it is a promising target for applications of statistical mechanics.

Is there a conserved quantity in economy? Drăgulescu and Yakovenko (2000) argue that such a conserved quantity is money m . Indeed, the ordinary economic agents can only receive money from and give money to other agents. They are not permitted to “manufacture” money, for example, to print dollar bills. When one agent i pays money Δm to another agent j for some goods or services, the money balances of the agents change as follows:

$$\begin{aligned} m_i &\rightarrow m'_i = m_i - \Delta m, \\ m_j &\rightarrow m'_j = m_j + \Delta m. \end{aligned} \quad (5)$$

The total amount of money of the two agents before and after the transaction remains the same,

$$m_i + m_j = m'_i + m'_j, \quad (6)$$

that is, there is a local conservation law for money. The rule (5) for the transfer of money is analogous to the transfer of energy from one molecule to another in molecular collisions in a gas, and (6) is analogous to conservation of energy in such collisions.

Addressing some misunderstandings developed in economic literature (Anglin 2005; Lux 2005; Gallegati et al. 2006; Lux 2008), we should emphasize that, in the model of Drăgulescu and Yakovenko (2000), the transfer of money from one agent to another happens voluntarily, as a payment for goods and services in a market economy. However, the model only keeps track of money flow, and does not keep track of what kinds of goods and service are delivered. One reason for this is that many goods, for example, food and other supplies, and most services, for example, getting a haircut or going to a movie, are not tangible and disappear after consumption. Because they are not conserved and also because they are measured in different physical units, it is not very practical to keep track of them. In contrast, money is measured in the same unit (within a given country with a single currency) and is conserved in transactions, so it is straightforward to keep track of money flow.

Unlike ordinary economic agents, a central bank or a central government can inject money into the economy. This process is analogous to an influx of energy into a system from external sources, for example, the Earth receives energy from the Sun. Dealing with these situations, physicists start with an idealization of a closed system in thermal equilibrium and then generalize to an open system subject to an energy flux. As long as the rate of money influx from central sources is slow compared with relaxation processes in the economy and does not cause hyperinflation, the system is in quasi-stationary statistical equilibrium with slowly changing parameters. This situation is analogous to heating a kettle on a gas stove slowly, where the kettle has a well-defined, but slowly increasing temperature at any moment of time.

Another potential problem with conservation of money is debt. This issue is discussed in more detail in section “[Models with Debt](#).” As a starting point, Drăgulescu and Yakovenko (2000) first considered simple models, where debt is not permitted. This means that money balances of agents cannot go below zero: $m_i \geq 0$ for all i . Transaction (5) takes place only when an agent has enough money to pay the price, $m_i \geq \Delta m$, otherwise the transaction does not take place. If an agent spends all the money, the balance drops to zero $m_i = 0$, so the agent cannot buy any goods from other agents. However, this agent can still produce goods or services, sell them to other agents, and receive money for them. In real life, cash balance dropping to zero is not at all unusual for people who live from paycheck to paycheck.

The conservation law is the key feature for the successful functioning of money. If the agents were permitted to “manufacture” money, they would be printing money and buying all goods for nothing, which would be a disaster. The physical medium of money is not essential, as long as the conservation law is enforced. Money may be in the form of paper cash, but today it is more often represented by digits in computerized bank accounts. The conservation law is the fundamental principle of accounting, whether in the single-entry or in the double-entry form. More discussion of banks and debt is given in section “[Models with Debt](#).”

The Boltzmann-Gibbs Distribution of Money

Having recognized the principle of money conservation, Drăgulescu and Yakovenko (2000) argued that the stationary distribution of money should be given by the exponential Boltzmann-Gibbs function analogous to (1):

$$P(m) = ce^{\frac{-m}{T_m}}. \quad (7)$$

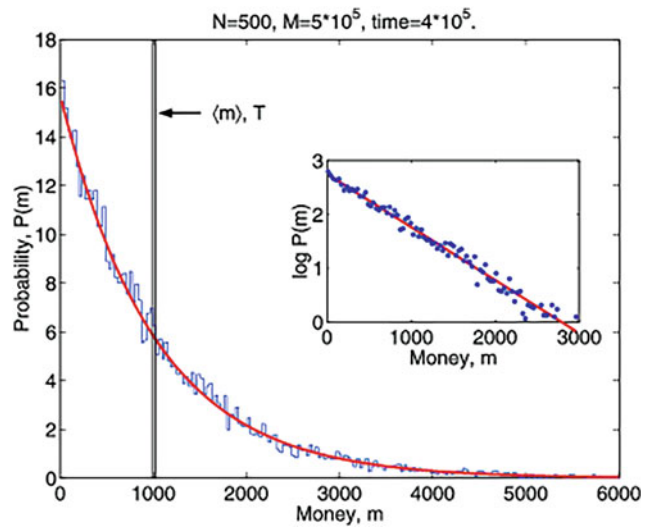
Here c is a normalizing constant, and T_m is the “money temperature,” which is equal to the average amount of money per agent: $T = \langle m \rangle = M/N$, where M is the total money, and N is the number of agents.

To verify this conjecture, Drăgulescu and Yakovenko (2000) performed agent-based computer simulations of money transfers between agents. Initially all agents were given the same amount of money, say, \$1000. Then, a pair of agents (i, j) were randomly selected, the amount Δm was transferred from one agent to another, and the process was repeated many times. Time evolution of the probability distribution of money $P(m)$ can be seen in computer animation videos at the Web pages (Computer animation videos of money-transfer models 2008; Wright 2007). After a transitory period, money distribution converges to the stationary form shown in Fig. 1. As expected, the distribution is very well fitted by the exponential function (7).

Several different rules for Δm were considered in Drăgulescu and Yakovenko (2000). In one model, the amount transferred was fixed to a constant $\Delta m = 1\$$. Economically, it means that all agents were selling their products for the same price $\Delta m = 1\$$. Computer animation (Computer animation videos of money-transfer models 2008) shows that the initial distribution of money first broadens to a symmetric, Gaussian curve, characteristic for a diffusion process. Then, the distribution starts to pile up around the $m = 0$ state, which acts as the impenetrable boundary, because of the imposed condition $m \geq 0$. As a result, $P(m)$ becomes skewed (asymmetric) and eventually reaches the stationary exponential shape, as shown in Fig. 1. The boundary at $m = 0$ is analogous to the ground-state energy in statistical physics. Without this boundary condition, the probability distribution of money would not

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Fig. 1 Stationary probability distribution of money $P(m)$ obtained in agent-based computer simulations. *Solid curves:* fits to the Boltzmann-Gibbs law (7). *Vertical lines:* the initial distribution of money. (Reproduced from Drăgulescu and Yakovenko (2000))



reach a stationary state. Computer animation (Computer animation videos of money-transfer models 2008; Wright 2007) also shows how the entropy of money distribution, defined as $S/N = -\sum_k P(m_k) \ln P(m_k)$, grows from the initial value $S = 0$, when all agents have the same money, to the maximal value at the statistical equilibrium.

While the model with $\Delta m = 1$ is very simple and instructive, it is not very realistic, because all prices are taken to be the same. In another model considered in Drăgulescu and Yakovenko (2000), Δm in each transaction is taken to be a random fraction of the average amount of money per agent, that is, $\Delta m = v(M/N)$, where v is a uniformly distributed random number between 0 and 1. The random distribution of Δm is supposed to represent the wide variety of prices for different products in the real economy. It reflects the fact that agents buy and consume many different types of products, some of them simple and cheap, some sophisticated and expensive. Moreover, different agents like to consume these products in different quantities, so there is variation in the amounts Δm paid, even though the unit price of the same product is constant. Computer simulation of this model produces exactly the same stationary distribution (7) as in the first model. Computer animation for this model is also available on the Web page (Computer animation videos of money-transfer models 2008).

The final distribution is universal despite different rules for Δm . To amplify this point further, Drăgulescu and Yakovenko (2000) also considered a toy model, where Δm was taken to be a random fraction of the average amount of money of the two agents: $\Delta m = v(m_i + m_j)/2$. This model produced the same stationary distribution (7) as the other two models.

The pairwise models of money transfer are attractive in their simplicity, but they represent a rather primitive market. The modern economy is dominated by big firms, which consist of many agents, so Drăgulescu and Yakovenko (2000) also studied a model with firms. One agent at a time is appointed to become a “firm.” The firm borrows capital K from another agent and returns it with interest hK , hires L agents and pays them wages W , manufactures Q items of a product, sells them to Q agents at price R , and receives profit $F = RQ - LW - hK$. All of these agents are randomly selected. The parameters of the model are optimized following a procedure from economics textbooks (McConnell and Brue 1996). The aggregate demand-supply curve for the product is used in the form $R(Q) = v/Q^\eta$, where Q is the quantity consumers would buy at price R , and η and v are some parameters. The production function of the firm has the traditional Cobb-Douglas form: $Q(L, K) = L^\chi K^{1-\chi}$, where χ is a parameter. Then the profit of the firm F is maximized with respect to K and L . The net result of the firm

activity is a many-body transfer of money, which still satisfies the conservation law. Computer simulation of this model generates the same exponential distribution (7), independently of the model parameters. The reasons for the universality of the Boltzmann-Gibbs distribution and its limitations are discussed from a different perspective in section “[Additive Versus Multiplicative Models](#).”

Well after paper (Drăgulescu and Yakovenko 2000) appeared, Italian econophysicists (Patriarca et al. 2005) found that similar ideas had been published earlier in obscure journals in Italian by Eleonora Bennati (Bennati 1988, 1993). They proposed calling these models the Bennati-Drăgulescu-Yakovenko game (Scalas et al. 2006). The Boltzmann distribution was independently applied to social sciences by Jürgen Mimkes using the Lagrange principle of maximization with constraints (Mimkes 2000, 2005). The exponential distribution of money was also found in Shubik (1999) using a Markov chain approach to strategic market games. A long time ago, Benoit Mandelbrot observed (see p. 83 in Mandelbrot (1960)):

There is a great temptation to consider the exchanges of money which occur in economic interaction as analogous to the exchanges of energy which occur in physical shocks between gas molecules.

He realized that this process should result in the exponential distribution, by analogy with the barometric distribution of density in the atmosphere. However, he discarded this idea, because it does not produce the Pareto power law, and proceeded to study the stable Lévy distributions. Ironically, the actual economic data, discussed in section “[Empirical Data on Money and Wealth Distributions](#)” and “[Empirical Data on Income Distribution](#),” do show the exponential distribution for the majority of the population. Moreover, the data have finite variance, so the stable Lévy distributions are not applicable because of their infinite variance.

Models with Debt

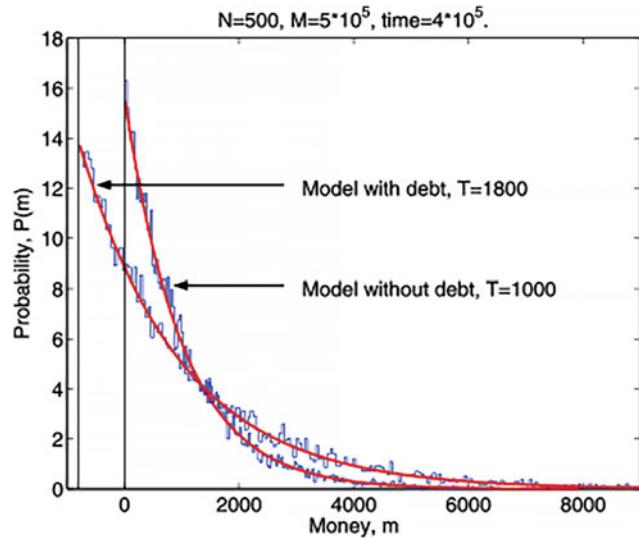
Now let us discuss how the results change when debt is permitted. Debt may be considered as negative money. When an agent borrows money from a bank (considered here as a big reservoir of money), the cash balance of the agent (positive money) increases, but the agent also acquires a

debt obligation (negative money), so the total balance (net worth) of the agent remains the same, and the conservation law of total money (positive and negative) is satisfied. After spending some cash, the agent still has the debt obligation, so the money balance of the agent becomes negative. Any stable economic system must have a mechanism preventing unlimited borrowing and unlimited debt. Otherwise, agents can buy any products without producing anything in exchange by simply going into unlimited debt. The exact mechanisms of limiting debt in the real economy are complicated and obscured. Drăgulescu and Yakovenko (2000) considered a simple model where the maximal debt of any agent is limited by a certain amount m_d . This means that the boundary condition $m_i \geq 0$ is now replaced by the condition $m_i \geq -m_d$ for all agents i . Setting interest rates on borrowed money to be zero for simplicity, Drăgulescu and Yakovenko (2000) performed computer simulations of the models described in section “[The Boltzmann-Gibbs Distribution of Money](#)” with the new boundary condition. The results are shown in Fig. 2. Not surprisingly, the stationary money distribution again has an exponential shape, but now with the new boundary condition at $m = -m_d$ and the higher money temperature $T_d = m_d + M/N$. By allowing agents to go into debt up to m_d , we effectively increase the amount of money available to each agent by m_d . So, the money temperature, which is equal to the average amount of effectively available money per agent, increases. A model with nonzero interest rates was also studied in Drăgulescu and Yakovenko (2000).

We see that debt does not violate the conservation law of money, but rather modifies boundary conditions for $P(m)$. When economics textbooks describe how “banks create money” or “debt creates money” (McConnell and Brue 1996), they count only positive money (cash) as money, but do not count liabilities (debt obligations) as negative money. With such a definition, money is not conserved. However, if we include debt obligations in the definition of money, then the conservation law is restored. This approach is in agreement with the principles of double-entry accounting, which records both assets and debts.

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Fig. 2 Stationary distributions of money with and without debt. The debt is limited to $m_d = 800$. *Solid curves*: fits to the Boltzmann-Gibbs laws with the “temperatures” $T = 1800$ and $T = 1000$. (Reproduced from Drăgulescu and Yakovenko (2000))



Debt obligations are as real as positive cash, as many borrowers painfully realized in their experience. A more detailed study of positive and negative money and bookkeeping from the point of view of econophysics is presented in a series of papers by the physicist Dieter Braun (2001; Fischer and Braun 2003a, b).

One way of limiting the total debt in the economy is the so-called required reserve ratio r (McConnell and Brue 1996). Every bank is required by law to set aside a fraction r of the money deposited with the bank, and this reserved money cannot be loaned further. If the initial amount of money in the system (the money base) is M_0 , then with loans and borrowing the total amount of positive money available to the agents increases to $M = M_0/r$, where the factor $1/r$ is called the money multiplier (McConnell and Brue 1996). This is how “banks create money.” Where does this extra money come from? It comes from the increase of the total debt in the system. The maximal total debt is equal to $D = M_0/r - M_0$ and is limited by the factor r . When the debt is maximal, the total amounts of positive, M_0/r , and negative, $M_0(1 - r)/r$, money circulate between the agents in the system, so there are effectively two conservation laws for each of them (Xi et al. 2005). Thus, we expect to see the exponential distributions of positive and negative money characterized by two different temperatures: $T_+ = M_0/rN$ and $T_- =$

$M_0(1 - r)/rN$. This is exactly what was found in computer simulations in Xi et al. (2005), shown in Fig. 3. Similar two-sided distributions were also found in Fischer and Braun (2003a).

Proportional Money Transfers and Saving Propensity

In the models of money transfer considered thus far, the transferred amount Δm is typically independent of the money balances of agents. A different model was introduced in the physics literature earlier (Ispolatov et al. 1998) under the name multiplicative asset exchange model. This model also satisfies the conservation law, but the amount of money transferred is a fixed fraction γ of the payer’s money in (5):

$$\Delta m = \gamma m_i. \quad (8)$$

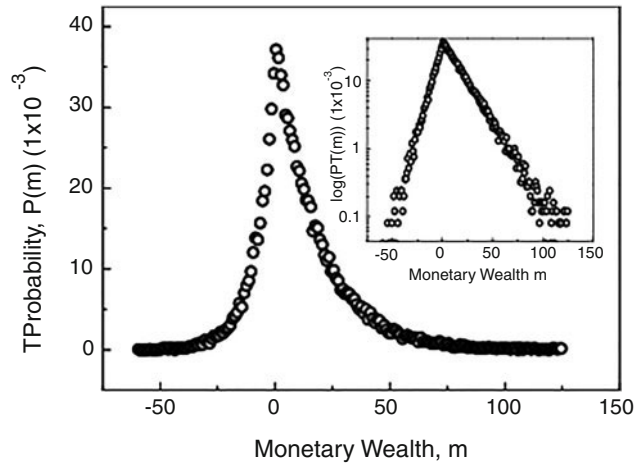
The stationary distribution of money in this model, shown in Fig. 4 with an exponential function, is close, but not exactly equal, to the Gamma distribution:

$$P(m) = cm^\beta e^{-\frac{m}{T}}. \quad (9)$$

Equation (9) differs from (7) by the power-law prefactor m^β . From the Boltzmann kinetic equation (discussed in more detail in section

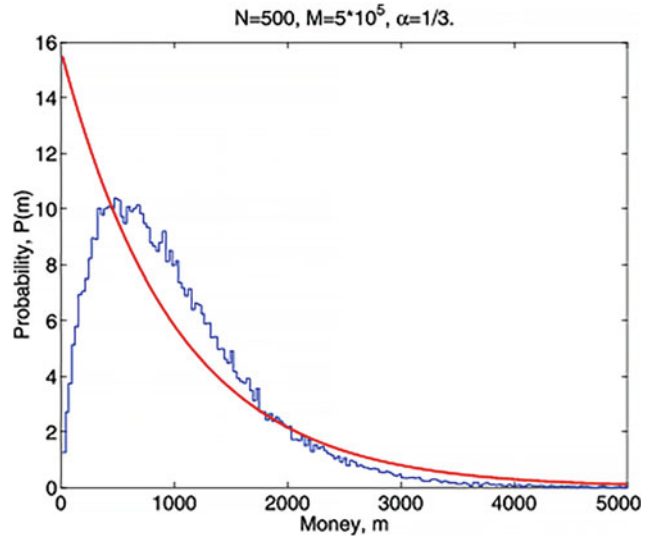
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Fig. 3 The stationary distribution of money for the required reserve ratio $r = 0.8$. The distribution is exponential for positive and negative money with different “temperatures” T_+ and T_- , as illustrated by the inset on log-linear scale. (Reproduced from Xi et al. (2005))



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Fig. 4 Stationary probability distribution of money in the multiplicative random exchange model (8) for $\gamma = 1/3$. Solid curve: the exponential Boltzmann-Gibbs law. (Reproduced from Drăgulescu and Yakovenko (2000))



“Additive Versus Multiplicative Models”), Ispolatov et al. (1998) derived a formula relating the parameters γ and β in (8) and (9):

$$\beta = \frac{-1 - \ln 2}{\ln(1 - \gamma)}. \quad (10)$$

When payers spend a relatively small fraction of their money $\gamma < 1/2$, (10) gives $\beta > 0$, so the low-money population is reduced and $P(m \rightarrow 0) = 0$, as shown in Fig. 4.

Later, Thomas Lux brought to the attention of physicists (Lux 2005) that essentially the same model, called the inequality process, had been introduced and studied much earlier by the

sociologist John Angle (1986, 1992a, b, 1996, 2002), see also the review Angle (2006) for additional references. While Ispolatov et al. (Ispolatov et al. 1998) did not give much justification for the proportionality law (8), Angle (1986) connected this rule with the surplus theory of social stratification (Engels 1972), which argues that inequality in human society develops when people can produce more than necessary for minimal subsistence. This additional wealth (surplus) can be transferred from original producers to other people, thus generating inequality. In the first paper by Angle (1986), the parameter γ was randomly distributed, and another parameter, δ , gave a higher probability of winning to the agent with a

higher money balance in (5). However, in the following papers, he simplified the model to a fixed γ (denoted as ω by Angle) and equal probabilities of winning for higher- and lower-balance agents, which makes it completely equivalent to the model of Ispolatov et al. (1998). Angle also considered a model (Angle 2002, 2006) where groups of agents have different values of γ , simulating the effect of education and other “human capital.” All of these models generate a Gamma-like distribution, well approximated by (9).

Another model with an element of proportionality was proposed in Chakraborti and Chakrabarti (2000). (This paper originally appeared as a follow-up preprint cond-mat/0004256 to the preprint cond-mat/0001432 of Drăgulescu and Yakovenko (2000).) In this model, the agents set aside (save) some fraction of their money λm_i , whereas the rest of their money balance $(1 - \lambda)m_i$ becomes available for random exchanges. Thus, the rule of exchange (5) becomes

$$\begin{aligned} m'_i &= \lambda m_i + \xi(1 - \lambda)(m_i + m_j), \\ m'_j &= \lambda m_j + (1 - \xi)(1 - \lambda)(m_i + m_j). \end{aligned} \quad (11)$$

Here the coefficient λ is called the saving propensity, and the random variable ξ is uniformly distributed between 0 and 1. It was pointed out in Angle (2006) that, by the change of notation $\lambda \rightarrow (1 - \gamma)$, (11) can be transformed to the same form as (8), if the random variable ξ takes only discrete values 0 and 1. Computer simulations (Chakraborti and Chakrabarti 2000) of the model (11) found a stationary distribution close to the Gamma distribution (9). It was shown that the parameter β is related to the saving propensity λ by the formula $\beta = 3\lambda/(1 - \lambda)$ (Patriarca et al. 2004a, b, 2005; Repetowicz et al. 2005). For $\lambda \neq 0$, agents always keep some money, so their balances never go to zero and $P(m \rightarrow 0) = 0$, whereas for $\lambda = 0$ the distribution becomes exponential.

In the subsequent papers by the Kolkata school (Chakrabarti 2005) and related papers, the case of random saving propensity was studied. In these models, the agents are assigned random parameters λ drawn from a uniform distribution between 0 and 1 (Chatterjee et al. 2004). It was found that

this model produces a power-law tail $P(m) \propto 1/m^2$ at high m . The reasons for stability of this law were understood using the Boltzmann kinetic equation (Repetowicz et al. 2005; Das and Yarlagadda 2005; Chatterjee et al. 2005), but most elegantly in the mean-field theory (Mohanty 2006). The fat tail originates from the agents whose saving propensity is close to 1, who hoard money and do not give it back (Patriarca et al. 2005, 2006). An interesting matrix formulation of the problem was presented in Gupta (2006). Patriarca et al. (2007) studied the relaxation rate in the money transfer models. Drăgulescu and Yakovenko (2000) studied a model with taxation, which also has an element of proportionality. The Gamma distribution was also studied for conservative models within a simple Boltzmann approach in Ferrero (2004) and using much more complicated rules of exchange in Scafetta et al. (2004a, b).

Additive Versus Multiplicative Models

The stationary distribution of money (9) for the models of section “Proportional Money Transfers and Saving Propensity” is different from the simple exponential formula (7) found for the models of section “The Boltzmann-Gibbs Distribution of Money.” The origin of this difference can be understood from the Boltzmann kinetic equation (Wannier 1987; Lifshitz and Pitaevskii 1981). This equation describes time evolution of the distribution function $P(m)$ due to pairwise interactions:

$$\begin{aligned} \frac{dP(m)}{dt} = & \iint \left\{ f_{[mm'] \rightarrow [mm'+]} P(m) P(m') \right. \\ & + f_{[mm'+] \rightarrow [mm']} P(m) \\ & \left. P(m' +) \right\} dm' d. \end{aligned} \quad (12)$$

Here $f_{[m,m'] \rightarrow [m-\Delta, m'+\Delta]}$ is the probability of transferring money Δ from an agent with money m to an agent with money m' per unit time. This probability, multiplied by the occupation numbers $P(m)$ and $P(m')$, gives the rate of transitions from the state $[m, m']$ to the state $[m - \Delta, m' + \Delta]$. The first term in (12) gives the depopulation rate of the state m . The second term in (12) describes the reverse process, where the occupation number

$P(m)$ increases. When the two terms are equal, the direct and reverse transitions cancel each other statistically, and the probability distribution is stationary: $dP(m)/dt = 0$. This is the principle of detailed balance.

In physics, the fundamental microscopic equations of motion of particles obey time-reversal symmetry. This means that the probabilities of the direct and reverse processes are exactly equal:

$$f_{[m,m'] \rightarrow [m-\Delta, m'+\Delta]} = f_{[m-\Delta, m'+\Delta] \rightarrow [m,m']}. \quad (13)$$

When (13) is satisfied, the detailed balance condition for (12) reduces to the equation $P(m)P(m') = P(m - \Delta)P(m' + \Delta)$, because the factors f cancel out. The only solution of this equation is the exponential function $P(m) = c \exp(-m/T_m)$, so the Boltzmann-Gibbs distribution is the stationary solution of the Boltzmann kinetic Eq. (12). Notice that the transition probabilities (13) are determined by the dynamical rules of the model, but the equilibrium Boltzmann-Gibbs distribution does not depend on the dynamical rules at all. This is the origin of the universality of the Boltzmann-Gibbs distribution. It shows that it may be possible to find out the stationary distribution without knowing details of the dynamical rules (which are rarely known very well), as long as the symmetry condition (13) is satisfied.

The models considered in section “[The Boltzmann-Gibbs Distribution of Money](#)” have the time-reversal symmetry. The model with the fixed money transfer Δ has equal probabilities (13) of transferring money from an agent with balance m to an agent with balance m' and vice versa. This is also true when Δ is random, as long as the probability distribution of Δ is independent of m and m' . Thus, the stationary distribution $P(m)$ is always exponential in these models.

However, there is no fundamental reason to expect time-reversal symmetry in economics, so (13) may be not valid. In this case, the system may have a nonexponential stationary distribution or no stationary distribution at all. In model (8), the time-reversal symmetry is broken. Indeed, when an agent i gives a fixed fraction γ of his money m_i to an agent with balance m_j , their balances become $(1 - \gamma)m_i$ and $m_j + \gamma m_i$. If we try to reverse this

process and appoint an agent j to be the payer and to give the fraction γ of her money, $\gamma(m_j + \gamma m_i)$, to agent i , the system does not return to the original configuration $[m_i, m_j]$. As emphasized by Angle (2006), the payer pays a deterministic fraction of his money, but the receiver receives a random amount from a random agent, so their roles are not interchangeable. Because the proportional rule typically violates the time-reversal symmetry, the stationary distribution $P(m)$ in multiplicative models is typically not exactly exponential. (However, when Δm is a fraction of the total money $m_i + m_j$ of the two agents, the model is time-reversible and has an exponential distribution, as discussed in section “[The Boltzmann-Gibbs Distribution of Money](#).”) Making the transfer dependent on the money balance of the payer effectively introduces a Maxwell’s demon into the model. That is why the stationary distribution is not exponential, and, thus, does not maximize entropy (4). Another view on the time-reversal symmetry in economic dynamics is presented in Ao (2007).

These examples show that the Boltzmann-Gibbs distribution does not hold for any conservative model. However, it is universal in a limited sense. For a broad class of models that have time-reversal symmetry, the stationary distribution is exponential and does not depend on the details of the model. Conversely, when the time-reversal symmetry is broken, the distribution may depend on the details of the model. The difference between these two classes of models may be rather subtle. Deviations from the Boltzmann-Gibbs law may occur only if the transition rates f in (13) explicitly depend on the agent’s money m or m' in an asymmetric manner. Drăgulescu and Yakovenko (2000) performed a computer simulation where the direction of payment was randomly selected in advance for every pair of agents (i, j) . In this case, money flows along directed links between the agents: $i \rightarrow j \rightarrow k$, and the time-reversal symmetry is strongly violated. This model is closer to the real economy, where one typically receives money from an employer and pays it to a grocery store. Nevertheless, the Boltzmann-Gibbs distribution was found in this model, because the transition rates f do not explicitly depend on m and m' and do not violate (13).

In the absence of detailed knowledge of real microscopic dynamics of economic exchanges, the semiuniversal Boltzmann-Gibbs distribution (7) is a natural starting point. Moreover, the assumption of Drăgulescu and Yakovenko (2000) that agents pay the same prices Δm for the same products, independent of their money balances m , seems very appropriate for the modern anonymous economy, especially for purchases over the Internet. There is no particular empirical evidence for the proportional rules (8) or (11). However, the difference between the additive (7) and multiplicative (9) distributions may be not so crucial after all. From the mathematical point of view, the difference is in the implementation of the boundary condition at $m = 0$. In the additive models of section “The Boltzmann-Gibbs Distribution of Money,” there is a sharp cutoff of $P(m)$ at $m = 0$. In the multiplicative models of section “Proportional Money Transfers and Saving Propensity,” the balance of an agent never reaches $m = 0$, so $P(m)$ vanishes at $m \rightarrow 0$ in a power-law manner. At the same time, $P(m)$ decreases exponentially for large m for both models.

By further modifying the rules of money transfer and introducing more parameters in the models, one can obtain even more complicated distributions (Scafetta and West 2007). However, one can argue that parsimony is the virtue of a good mathematical model, not the abundance of additional assumptions and parameters, whose correspondence to reality is hard to verify.

Statistical Mechanics of Wealth Distribution

In the econophysics literature on exchange models, the terms “money” and “wealth” are often used interchangeably; however, economists emphasize the difference between these two concepts. In this section, we review the models of wealth distribution, as opposed to money distribution.

Models with a Conserved Commodity

What is the difference between money and wealth? One can argue (Drăgulescu and Yakovenko 2000) that wealth w_i is equal to money m_i plus the other

property that an agent i has. The latter may include durable material property, such as houses and cars, and financial instruments, such as stocks, bonds, and options. Money (paper cash, bank accounts) is generally liquid and countable. However, the other property is not immediately liquid and has to be sold first (converted into money) to be used for other purchases. In order to estimate the monetary value of property, one needs to know the price p . In the simplest model, let us consider just one type of property, say, stocks s . Then the wealth of an agent i is given by the formula

$$w_i = m_i + ps_i. \quad (14)$$

It is assumed that the price p is common for all agents and is established by some kind of market process, such as an auction, and may change in time.

It is reasonable to start with a model where both the total money $M = \sum_i m_i$ and the total stock $S = \sum_i s_i$ are conserved (Chakraborti et al.

2001; Chatterjee and Chakrabarti 2006; Ausloos and Pekalski 2007). The agents pay money to buy stock and sell stock to get money, and so on. Although M and S are conserved, the total wealth $W = \sum_i w_i$ is generally not conserved,

because of the price fluctuation (Chatterjee and Chakrabarti 2006) in (14). This is an important difference from the money transfer models of section “Statistical Mechanics of Money Distribution.” Here the wealth w_i of an agent i , not participating in any transactions, may change when transactions between other agents establish a new price p . Moreover, the wealth w_i of an agent i does not change after a transaction with an agent j . Indeed, in exchange for paying money Δm , agent i receives the stock $\Delta s = \Delta m/p$, so her total wealth (14) remains the same. In principle, the agent can instantaneously sell the stock back at the same price and recover the money paid. If the price p never changes, then the wealth w_i of each agent remains constant, despite transfers of money and stock between agents.

We see that redistribution of wealth in this model is directly related to price fluctuations.

One mathematical model of this process was studied in Silver et al. (2002). In this model, the agents randomly change preferences for the fraction of their wealth invested in stocks. As a result, some agents offer stock for sale and some want to buy it. The price p is determined from the market-clearing auction matching supply and demand. Silver et al. (Silver et al. 2002) demonstrated in computer simulations and proved analytically using the theory of Markov processes that the stationary distribution $P(w)$ of wealth w in this model is given by the Gamma distribution, as in (9). Various modifications of this model (Lux 2005), such as introducing monopolistic coalitions, do not change this result significantly, which shows the robustness of the Gamma distribution. For models with a conserved commodity, Chatterjee and Chakrabarti (2006) found the Gamma distribution for a fixed saving propensity and a power law tail for a distributed saving propensity.

Another model with conserved money and stock was studied in Raberto et al. (2003) for an artificial stock market where traders follow different investment strategies: random, momentum, contrarian, and fundamentalist. Wealth distribution in the model with random traders was found have a power-law tail $P(w) \sim 1/w^2$ for large w . However, unlike in most other simulation, where all agents initially have equal balances, here the initial money and stock balances of the agents were randomly populated according to a power law with the same exponent. This raises the question whether the observed power-law distribution of wealth is an artifact of the initial conditions, because equilibration of the upper tail may take a very long simulation time.

Models with Stochastic Growth of Wealth

Although the total wealth W is not exactly conserved in the models considered in section “Models with a Conserved Commodity,” W nevertheless remains constant on average, because the total money M and stock S are conserved. A different model for wealth distribution was proposed in Bouchaud and Mézard (2000). In this model, time evolution of the wealth w_i of an agent i is given by the stochastic differential equation

$$\frac{dw_i}{dt} = \eta_i(t)w_i + \sum_{j(\neq i)} J_{ij}w_j - \sum_{j(\neq i)} J_{ji}w_i, \quad (15)$$

where $\eta_i(t)$ is a Gaussian random variable with mean $\langle \eta \rangle$ and variance $2\sigma^2$. This variable represents growth or loss of wealth of an agent due to investment in stock market. The last two terms describe transfer of wealth between different agents, which is taken to be proportional to the wealth of the payers with the coefficients J_{ij} . So, the model (15) is multiplicative and invariant under the scale transformation $w_i \rightarrow Zw_i$. For simplicity, the exchange fractions are taken to be the same for all agents: $J_{ij} = J/N$ for all $i \neq j$, where N is the total number of agents. In this case, the last two terms in (15) can be written as $J(\langle w \rangle - w_i)$, where $\langle w \rangle = \sum_i w_i/N$ is the average wealth

per agent. This case represents a “mean-field” model, where all agents feel the same environment. It can be easily shown that the average wealth increases in time as $\langle w \rangle_t = \langle w \rangle_0 e^{(\langle \eta \rangle + \sigma^2)t}$. Then, it makes more sense to consider the relative wealth $\tilde{w}_i = w_i/\langle w \rangle_t$. Equation (15) for this variable becomes

$$\frac{d\tilde{w}_i}{dt} = (\eta_i(t) - \langle \eta \rangle - \sigma^2)\tilde{w}_i + J(1 - \tilde{w}_i). \quad (16)$$

The probability distribution $P(\tilde{w}, t)$ for the stochastic differential Eq. (16) is governed by the Fokker-Planck equation:

$$\frac{\partial P}{\partial t} = \frac{\partial [J(\tilde{w} - 1) + \sigma^2 \tilde{w}]P}{\partial \tilde{w}} + \sigma^2 \frac{\partial}{\partial \tilde{w}} \left(\tilde{w} \frac{\partial (\tilde{w}P)}{\partial \tilde{w}} \right). \quad (17)$$

The stationary solution ($\partial P/\partial t = 0$) of this equation is given by the following formula:

$$P(\tilde{w}) = c \frac{e^{-\frac{J}{\sigma^2 \tilde{w}}}}{\tilde{w}^{\frac{2+J}{\sigma^2}}}. \quad (18)$$

The distribution (18) is quite different from the Boltzmann-Gibbs (7) and Gamma (9) distributions. Equation (18) has a power-law tail at large $\tilde{w}$ and a sharp cutoff at small $\tilde{w}$. Equation (15) is a version of the generalized Lotka-Volterra model,

and the stationary distribution (18) was also obtained in Solomon and Richmond (2001, 2002). The model was generalized to include negative wealth in Huang (2004).

Bouchaud and Mézard (2000) used the mean-field approach. A similar result was found for a model with pairwise interaction between agents in Slanina (2004). In this model, wealth is transferred between the agents using the proportional rule (8). In addition, the wealth of the agents increases by the factor $1 + \zeta$ in each transaction. This factor is supposed to reflect creation of wealth in economic interactions. Because the total wealth in the system increases, it makes sense to consider the distribution of relative wealth $P(\tilde{w})$. In the limit of continuous trading, Slanina (2004) found the same stationary distribution (18). This result was reproduced using a mathematically more involved treatment of this model in Cordier et al. (2005). Numerical simulations of the models with stochastic noise η in Scafetta et al. (2004a, b) also found a power-law tail for large w .

Let us contrast the models discussed in section “Models with a Conserved Commodity” and “Models with Stochastic Growth of Wealth.” In the former case, where money and commodity are conserved and wealth does not grow, the distribution of wealth is given by the Gamma distribution with an exponential tail for large w . In the latter models, wealth grows in time exponentially, and the distribution of relative wealth has a power-law tail for large $\tilde{w}$. These results suggest that the presence of a power-law tail is a nonequilibrium effect that requires constant growth or inflation of the economy, but disappears for a closed system with conservation laws.

Reviews of the models discussed were also given in Richmond et al. (2006a, b). Because of lack of space, we omit discussion of models with wealth condensation (Bouchaud and Mézard 2000; Ispolatov et al. 1998; Burda et al. 2002; Pianegonda et al. 2003; Braun 2006), where a few agents accumulate a finite fraction of the total wealth, and studies of wealth distribution on networks (Coelho et al. 2005; Iglesias et al. 2003; Di Matteo et al. 2004; Hu et al. 2007). Here we discuss the models with long-range

interaction, where any agent can exchange money and wealth with any other agent. A local model, where agents trade only with the nearest neighbors, was studied in Bak et al. (1999).

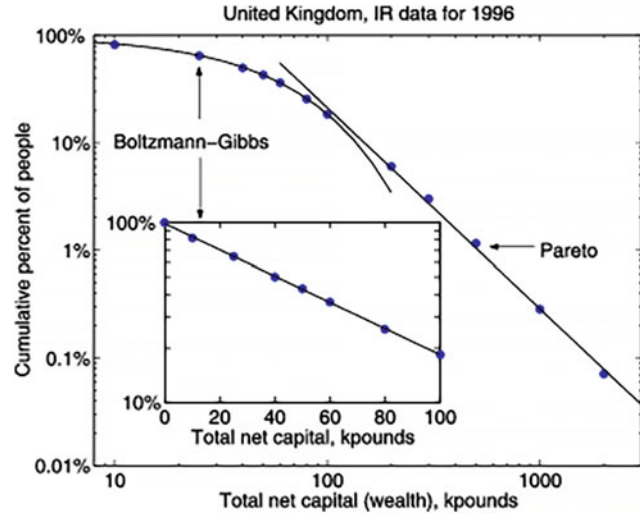
Empirical Data on Money and Wealth Distributions

It would be very interesting to compare theoretical results for money and wealth distributions in various models with empirical data. Unfortunately, such empirical data are difficult to find. Unlike income, which is discussed in section “Data and Models for Income Distribution,” wealth is not routinely reported by the majority of individuals to the government. However, in many countries, when a person dies, all assets must be reported for the purpose of inheritance tax. So, in principle, there exist good statistics of wealth distribution among dead people, which, of course, is different from the wealth distribution among living people. Using an adjustment procedure based on the age, gender, and other characteristics of the deceased, the UK tax agency, the Inland Revenue, reconstructed the wealth distribution of the whole population of the UK (Revenue and Customs 2003). Figure 5 shows the UK data for 1996 reproduced from Drăgulescu and Yakovenko (2001a). The figure shows the cumulative probability $C(w) = \int_w^\infty P(w')dw'$ as a function of the personal net wealth w , which is composed of assets (cash, stocks, property, household goods, etc.) and liabilities (mortgages and other debts). Because statistical data are usually reported at nonuniform intervals of w , it is more practical to plot the cumulative probability distribution $C(w)$ rather than its derivative, the probability density $P(w)$. Fortunately, when $P(w)$ is an exponential or a power-law function, then $C(w)$ is also an exponential or a power-law function.

The cumulative probability distribution in Fig. 5 is plotted on a log-log scale, where a straight line represents a power-law dependence. The figure shows that the distribution follows a power law $C(w) \propto 1/w^\alpha$ with exponent $\alpha = 1.9$ for wealth greater than about £100,000. The inset in Fig. 5 shows the data on log-linear scale, where the straight line represents an exponential dependence. We observe that below £100,000 the data

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Fig. 5 Cumulative probability distribution of net wealth in the UK shown on log-log and log-linear (inset) scales. Points represent the data from the Inland Revenue, and solid lines are fits to the exponential (Boltzmann-Gibbs) and power (Pareto) laws. (Reproduced from (Drăgulescu and Yakovenko 2001a))



are well fitted by the exponential distribution $C(w) \propto \exp(-w/T_w)$ with the effective “wealth temperature” $T_w = £60,000$ (which corresponds to the median wealth of £41,000). So, the distribution of wealth is characterized by the Pareto power law in the upper tail of the distribution and the exponential Boltzmann-Gibbs law in the lower part of the distribution for the great majority (about 90%) of the population. Similar results are found for the distribution of income, as discussed in section “[Data and Models for Income Distribution](#).” One may speculate that the wealth distribution in the lower part is dominated by distribution of money, because the corresponding people do not have other significant assets, so the results of section “[Statistical Mechanics of Money Distribution](#)” give the Boltzmann-Gibbs law. On the other hand, the upper tail of the wealth distribution is dominated by investment assets, where the results of section “[Models with Stochastic Growth of Wealth](#)” give the Pareto law. The power law was studied by many researchers for the upper-tail data, such as the Forbes list of the 400 richest people (Klass et al. 2007; Sinha 2006), but much less attention was paid to the lower part of the wealth distribution. Curiously, Abdul-Magd (2002) found that the wealth distribution in ancient Egyptian society was consistent with (18).

For direct comparison with the results of section “[Statistical Mechanics of Money Distribution](#),” it would be very interesting to find data on

the distribution of money, as opposed to the distribution of wealth. Making a reasonable assumption that most people keep most of their money in banks, one can approximate the distribution of money by the distribution of balances on bank accounts. (Balances on all types of bank accounts, such as checking, saving, and money manager, associated with the same person should be added up.) Despite imperfections (people may have accounts with different banks or not keep all their money in banks), the distribution of balances on bank accounts would give valuable information about the distribution of money. The data for a big enough bank would be representative of the distribution in the whole economy. Unfortunately, it has not been possible to obtain such data thus far, even though it would be completely anonymous and not compromise the privacy of bank clients.

Measuring the probability distribution of money would be very useful, because it determines how much people can, in principle, spend on purchases without going into debt. This is different from the distribution of wealth, where the property component, such as house, car, or retirement investment, is effectively locked up and, in most cases, is not easily available for consumer spending. So, although wealth distribution may reflect the distribution of economic power, the distribution of money is more relevant for consumption. Money distribution can be

useful for determining prices that maximize revenue of a manufacturer (Drăgulescu and Yakovenko 2000). If a price p is set too high, few people can afford it, and, if a price is too low, the sales revenue is small, so the optimal price must be in-between. The fraction of the population who can afford to pay the price p is given by the cumulative probability $C(p)$, so the total sales revenue is proportional to $pC(p)$. For the exponential distribution $C(p) = \exp(-p/T_m)$, the maximal revenue is achieved at $p = T_m$, that is, at the optimal price equal to the average amount of money per person (Drăgulescu and Yakovenko 2000). Indeed, the prices of mass-market consumer products, such as computers, electronics goods, and appliances, remain stable for many years at a level determined by their affordability to the population, whereas the technical parameters of these products at the same price level improve dramatically owing to technological progress.

Data and Models for Income Distribution

In contrast to money and wealth distributions, a lot more empirical data are available for the distribution of income r from tax agencies and population surveys. In this section, we first present empirical data on income distribution and then discuss theoretical models.

Empirical Data on Income Distribution

Empirical studies of income distribution have a long history in the economics literature (Kakwani 1980; Champenowne and Cowell 1998; Atkinson and Bourguignon 2000). Following the work by Pareto (1897), much attention was focused on the power-law upper tail of the income distribution and less on the lower part. In contrast to more complicated functions discussed in the literature, Drăgulescu and Yakovenko (2001b) introduced a new idea by demonstrating that the lower part of income distribution can be well fitted with a simple exponential function $P(r) = c \exp(-r/T_r)$ characterized by just one parameter, the “income temperature” T_r . Then it was recognized that the whole income distribution can be

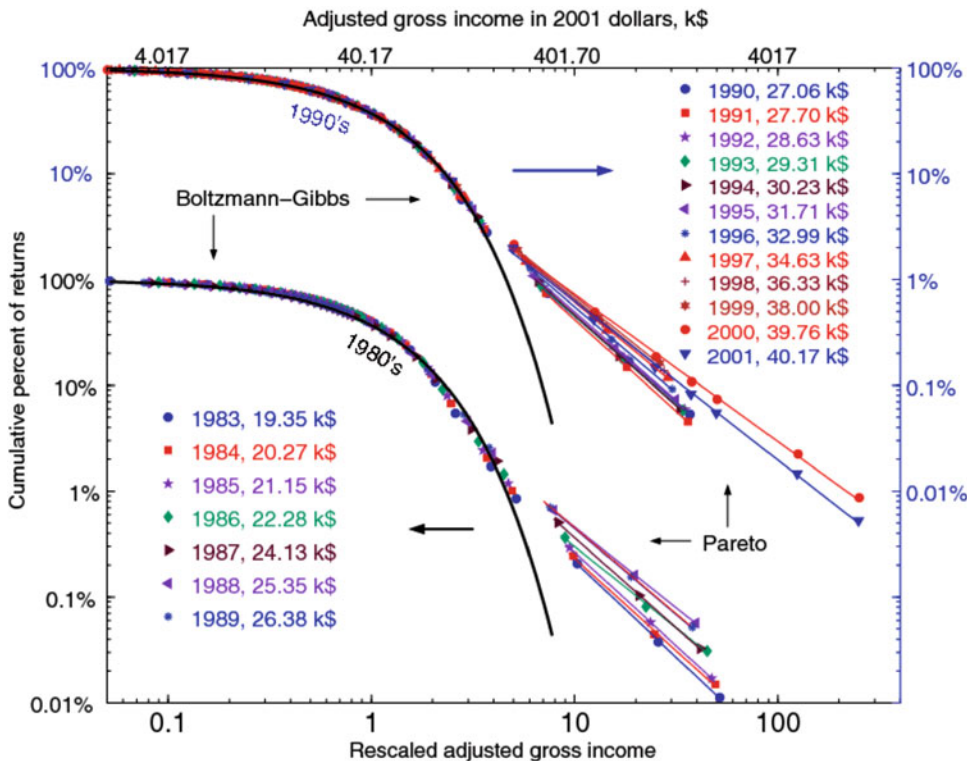
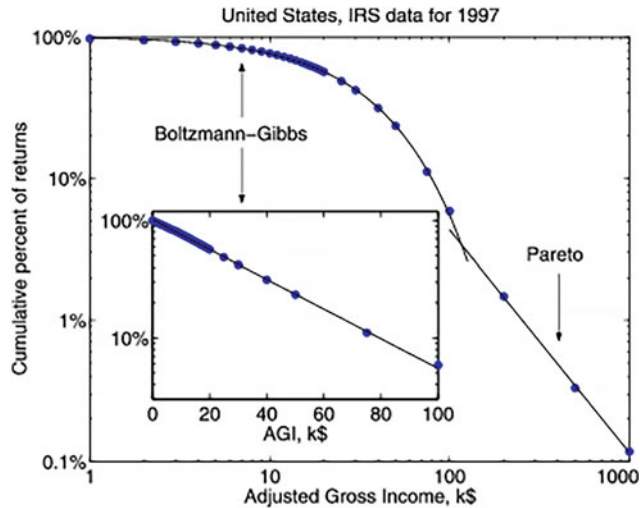
fitted by an exponential function in the lower part and a power-law function in the upper part (Drăgulescu and Yakovenko 2001a, 2003), as shown in Fig. 6. The straight line on the log-linear scale in the inset of Fig. 6 demonstrates the exponential Boltzmann-Gibbs law, and the straight line on the log-log scale in the main panel illustrates the Pareto power law. The fact that income distribution consists of two distinct parts reveals the two-class structure of American society (Yakovenko and Silva 2005; Silva and Yakovenko 2005). Coexistence of the exponential and power-law distributions is known in plasma physics and astrophysics, where they are called the “thermal” and “superthermal” parts (Hasegawa et al. 1985; Desai et al. 2003; Collier 2004). The boundary between the lower and upper classes can be defined as the intersection point of the exponential and power-law fits in Fig. 6. For 1997, the annual income separating the two classes was about \$120,000. About 3% of the population belonged to the upper class, and 97% belonged to the lower class.

Silva and Yakovenko (2005) studied time evolution of income distribution in the USA during 1983–2001 on the basis of data from the Internal Revenue Service (IRS), the government tax agency. The structure of the income distribution was found to be qualitatively the same for all years, as shown in Fig. 7. The average income in nominal dollars approximately doubled during this time interval. So, the horizontal axis in Fig. 7 shows the normalized income r/T_r , where the “income temperature” T_r was obtained by fitting of the exponential part of the distribution for each year. The values of T_r are shown in Fig. 7. The plots for the 1980s and 1990s are shifted vertically for clarity. We observe that the data points in the lower-income part of the distribution collapse on the same exponential curve for all years. This demonstrates that the shape of the income distribution for the lower class is extremely stable and does not change in time, despite the gradual increase of the average income in nominal dollars. This observation suggests that the lower-class distribution is in statistical, “thermal” equilibrium.

On the other hand, Fig. 7 shows that the income distribution in the upper class does not

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Fig. 6 Cumulative probability distribution of tax returns for the USA in 1997 shown on log-log and log-linear (*inset*) scales. Points represent the Internal Revenue Service (IRS) data, and *solid lines* are fits to the exponential and power-law functions. (Reproduced from (Drăgulescu and Yakovenko 2003))



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Fig. 7 Cumulative probability distribution of tax returns plotted on log-log scale versus r/T_r (the annual income r normalized by the average income T_r in the exponential

part of the distribution). The IRS data points are for 1983–2001, and the *columns of numbers* give the values of T_r for the corresponding years. (Reproduced from Silva and Yakovenko (2005))

rescale and significantly changes in time. Silva and Yakovenko (2005) found that the exponent α of the power law $C(r) \propto 1/r^\alpha$ decreased from 1.8 in 1983 to 1.4 in 2000. This means that the upper tail

became “fatter.” Another useful parameter is the total income of the upper class as the fraction f of the total income in the system. The fraction f increased from 4% in 1983 to 20% in 2000

(Silva and Yakovenko 2005). However, in 2001, α increased and f decreased, indicating that the upper tail was reduced after the stock market crash at that time. These results indicate that the upper tail is highly dynamical and not stationary. It tends to swell during the stock market boom and shrink during the bust. Similar results were found for Japan (Souma 2001, 2002; Fujiwara et al. 2003; Aoyama et al. 2003).

Although relative income inequality within the lower class remains stable, the overall income inequality in the USA has increased significantly as a result of the tremendous growth of the income of the upper class. This is illustrated by the Lorenz curve and the Gini coefficient shown in Fig. 8. The Lorenz curve (Kakwani 1980) is a standard way of representing income distribution in the economics literature. It is defined in terms of two coordinates $x(r)$ and $y(r)$ depending on a parameter r :

$$\begin{aligned} x(r) &= \int_0^r P(r') dr', \\ y(r) &= \frac{\int_0^r r' P(r') dr'}{\int_0^\infty r' P(r') dr'}. \end{aligned} \quad (19)$$

The horizontal coordinate $x(r)$ is the fraction of the population with income below r , and the vertical coordinate $y(r)$ is the fraction of the income this population accounts for. As r changes from 0 to ∞ , x and y change from 0 to 1 and parametrically define a curve in the (x, y) -plane.

Figure 8 shows the data points for the Lorenz curves in 1983 and 2000, as computed by the IRS (Strudler et al. 2003). Drăgulescu and Yakovenko (2001b) analytically derived the Lorenz curve formula $y = x + (1 - x) \ln(1 - x)$ for a purely exponential distribution $P(r) = c \exp(-r/T_r)$. This formula is shown by the red line in Fig. 8 and describes the 1983 data reasonably well. However, for 2000, it is essential to take into account the fraction f of income in the upper tail, which modifies the Lorenz formula as follows (Drăgulescu and Yakovenko 2003; Yakovenko and Silva 2005; Silva and Yakovenko 2005):

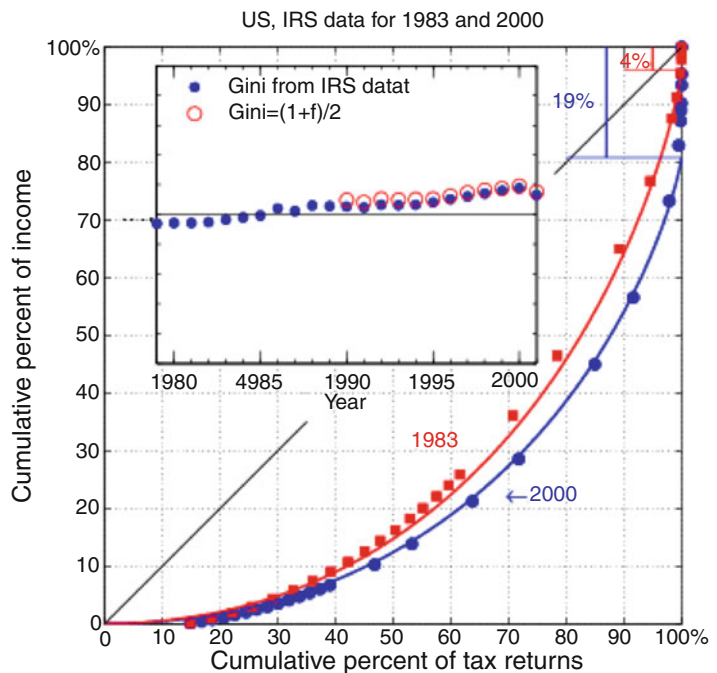
$$y = (1 - f)[x + (1 - x) \ln(1 - x)] + f\Theta(x - 1). \quad (20)$$

The last term in (20) represent the vertical jump of the Lorenz curve at $x = 1$, where a very small percentage of the population in the upper class

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Fig. 8 Lorenz plots for income distribution in 1983 and 2000. The data points are from the IRS (Strudler et al. 2003), and the theoretical curves represent (20) with f from Fig. 7. *Inset:* The closed circles are the IRS data 113 for the Gini coefficient G , and the open circles show the theoretical formula $G = (1 + f)/2$. (Reproduced from Silva and Yakovenko (2005))



accounts for a substantial fraction f of the total income. The blue curve representing (20) fits the 2000 data in Fig. 8 very well.

The deviation of the Lorenz curve from the straight diagonal line in Fig. 8 is a certain measure of income inequality. Indeed, if everybody had the same income, the Lorenz curve would be a diagonal line, because the fraction of income would be proportional to the fraction of the population. The standard measure of income inequality is the so-called Gini coefficient $0 \leq G \leq 1$, which is defined as the area between the Lorenz curve and the diagonal line, divided by the area of the triangle beneath the diagonal line (Kakwani 1980). Time evolution of the Gini coefficient, as computed by the IRS (Strudler et al. 2003), is shown in the inset of Fig. 8. Drăgulescu and Yakovenko (2001b) derived analytically the result that $G = 1/2$ for a purely exponential distribution. In the first approximation, the values of G shown in the inset of Fig. 8 are indeed close to the theoretical value $1/2$. If we take into account the upper tail using (20), the formula for the Gini coefficient becomes $G = (1 + f)/2$ (Silva and Yakovenko 2005). The inset in Fig. 8 shows that this formula is a very good fit to the IRS data for the 1990s using the values of f deduced from Fig. 7. The values $G < 1/2$ for the 1980s cannot be captured by this formula, because the Lorenz data points are slightly above the theoretical curve for 1983 in

Fig. 8. Overall, we observe that income inequality has been increasing for the last 20 years, because of swelling of the Pareto tail, but decreased in 2001 after the stock market crash.

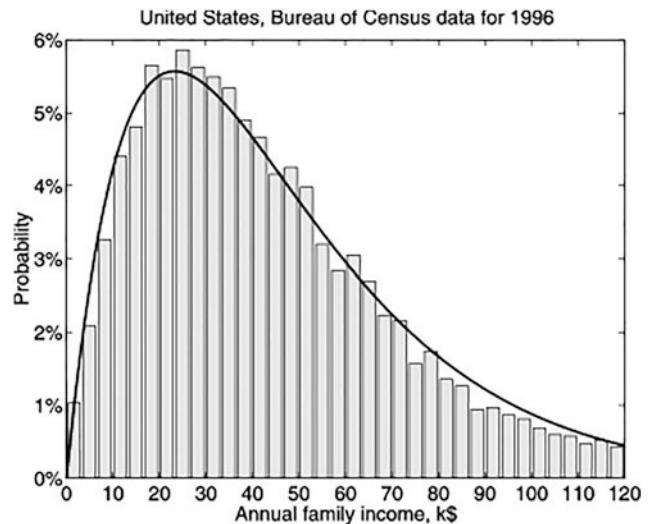
Thus far we have discussed the distribution of individual income. An interesting related question is the distribution $P_2(r)$ of family income $r = r_1 + r_2$, where r_1 and r_2 are the incomes of spouses. If individual incomes are distributed exponentially $P(r) \propto \exp(-r/T_r)$, then

$$\begin{aligned} P_2(r) &= \int_0^r dr' P(r') P(r - r') \\ &= cr \exp(-r/T_r), \end{aligned} \quad (21)$$

where c is a normalization constant. Figure 9 shows that (21) is in good agreement with the family income distribution data from the US Census Bureau (Drăgulescu and Yakovenko 2001b). In (21), we assumed that incomes of spouses are uncorrelated. This simple approximation is indeed supported by the scatter plot of incomes of spouses shown in Fig. 10. Each family is represented in this plot by two points (r_1, r_2) and (r_2, r_1) for symmetry. We observe that the density of points is approximately constant along the lines of constant family income $r_1 + r_2 = \text{const}$, which indicates that incomes of spouses are approximately uncorrelated. There is no significant

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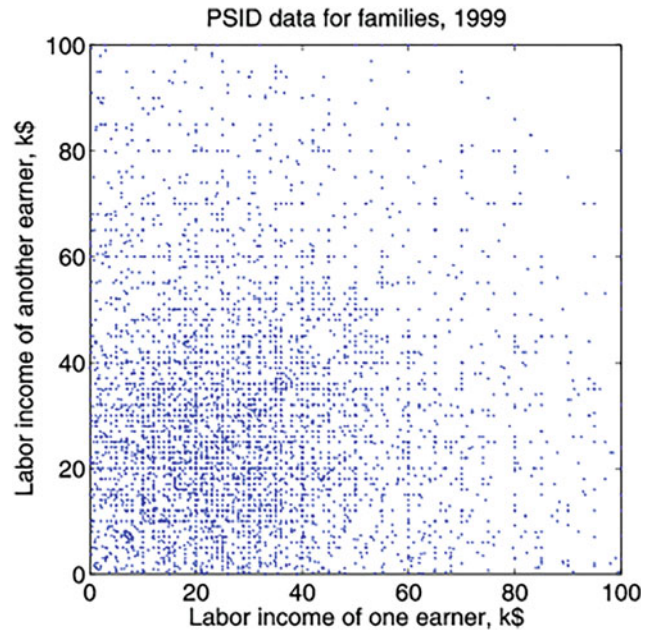
Fig. 9 Probability distribution of family income for families with two adults (US Census Bureau data). *Solid line:* fit to (21). (Reproduced from Drăgulescu and Yakovenko (2001b))



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Fig. 10 Scatter plot of the spouses' incomes (r_1, r_2) and (r_2, r_1) based on the data from the Panel Study of Income Dynamics (PSID). (Reproduced from Drăgulescu and Yakovenko (2003))



clustering of points along the diagonal $r_1 = r_2$, that is, no strong positive correlation of spouses' incomes.

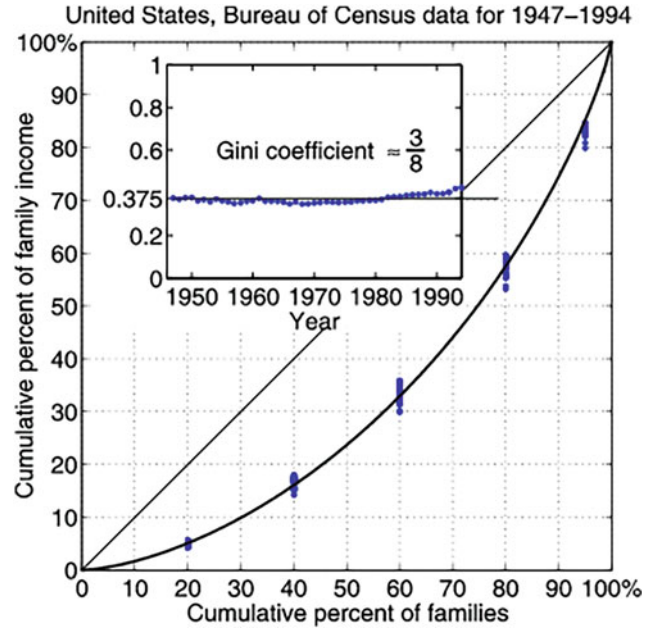
The Gini coefficient for the family income distribution (21) was calculated in Drăgulescu and Yakovenko (2001b) as $G = 3/8 = 37.5\%$. Figure 11 shows the Lorenz quintiles and the Gini coefficient for 1947–1994 plotted from the US Census Bureau data. The solid line, representing the Lorenz curve calculated from (21), is in good agreement with the data. The systematic deviation for the top 5% of earners results from the upper tail, which has a less pronounced effect on family income than on individual income, because of income averaging in the family. The Gini coefficient, shown in the inset of Fig. 11, is close to the calculated value of 37.5%. Moreover, the average G for the developed capitalist countries of North America and western Europe, as determined by the World Bank (Drăgulescu and Yakovenko 2003), is also close to the calculated value of 37.5%.

Income distribution has been examined in econophysics papers for different countries: Japan (Ferrero 2004; Souma 2001, 2002; Fujiwara et al. 2003; Aoyama et al. 2003; Souma and Nirei 2005, Nirei and Souma 2007; Ferrero 2005), Germany (Clementi and Gallegati 2005a;

Clementi et al. 2007), the UK (Ferrero 2004, 2005; Richmond et al. 2006b; Clementi and Gallegati 2005a; Clementi et al. 2007), Italy (Clementi et al. 2007; Clementi and Gallegati 2005b; Clementi et al. 2006), the USA (Clementi and Gallegati 2005a; Rawlings et al. 2004), India (Sinha 2006), Australia (Di Matteo et al. 2004; Clementi et al. 2006; Banerjee et al. 2006), and New Zealand (Ferrero 2004, 2005). The distributions are qualitatively similar to the results presented in this section. The upper tail follows a power law and comprises a small fraction of the population. To fit the lower part of the distribution, the use of exponential, Gamma, and log-normal distributions was reported in different papers. Unfortunately, income distribution is often reported by statistical agencies for households, so it is difficult to differentiate between one-earner and two-earner income distributions. Some papers reported the use of interpolating functions with different asymptotic behavior for low and high incomes, such as the Tsallis function (Ferrero 2005) and the Kaniadakis function (Clementi et al. 2007). However, the transition between the lower and upper classes is not smooth for the US data shown in Figs. 6 and 7, so such functions would not be useful in this case. The

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Fig. 11 Lorenz plot for family income calculated from (21), compared with the US Census data points. *Inset:* The US Census data points for the Gini coefficient for families, compared with the theoretically calculated value $3/8=37.5\%$. (Reproduced from Drăgulescu and Yakovenko (2001b))



special case is income distribution in Argentina during the economic crisis, which shows a time-dependent bimodal shape with two peaks (Ferrero 2005).

Theoretical Models of Income Distribution

Having examined the empirical data on income distribution, let us now discuss theoretical models. Income r_i is the influx of money per unit time to an agent i . If the money balance m_i is analogous to energy, then the income r_i would be analogous to power, which is the energy flux per unit time. So, one should conceptually distinguish between the distributions of money and income. While money is regularly transferred from one agent to another in pairwise transactions, it is not typical for agents to trade portions of their income. Nevertheless, indirect transfer of income may occur when one employee is promoted and another demoted, while the total annual budget is fixed, or when one company gets a contract, whereas another one loses it, etc. A reasonable approach, which has a long tradition in the economics literature (Gibrat 1931; Kalecki 1945; Champenowne 1953), is to treat individual income r as a stochastic process and study its probability distribution. In general, one can study a Markov process generated by a matrix of

transitions from one income to another. In the case where income r changes by a small amount Δr over a time period Δt , the Markov process can be treated as income diffusion. Then one can apply the general Fokker-Planck equation (Lifshitz and Pitaevskii 1981) to describe evolution in time t of the income distribution function $P(r, t)$ (Silva and Yakovenko 2005):

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial r} \left[AP + \frac{\partial(BP)}{\partial r} \right], \quad (22)$$

$$A = -\frac{\langle \Delta r \rangle}{\Delta t}, \quad B = \frac{\langle (\Delta r)^2 \rangle}{2\Delta t}.$$

The coefficients A and B in (22) are determined by the first and second moments of income changes per unit time. The stationary solution $\partial_t P = 0$ of (22) obeys the following equation with the general solution:

$$\frac{\partial(BP)}{\partial r} = -AP,$$

$$P(r) = \frac{c}{B(r)} \exp \left(-\int^r \frac{A(r')}{B(r')} dr' \right). \quad (23)$$

For the lower part of the distribution, it is reasonable to assume that Δr is independent of r ,

that is, the changes of income are independent of income itself. This process is called additive diffusion (Silva and Yakovenko 2005). In this case, the coefficients in (22) are constants A_0 and B_0 . Then (23) gives the exponential distribution $P(r) \propto \exp(-r/T_r)$, with the effective income temperature $T_r = B_0/A_0$. Notice that a meaningful stationary solution (23) requires that $A > 0$, that is, $\langle \Delta r \rangle < 0$. The coincidence of this result with the Boltzmann-Gibbs exponential law (1) and (7) is not accidental. Indeed, instead of considering pairwise interaction between particles, one can derive (1) by considering energy transfers between a particle and a big reservoir, as long as the transfer process is “additive” and does not involve a Maxwell-demon-like discrimination. Stochastic income fluctuations are described by a similar process. So, although money and income are different concepts, they may have similar distributions, because they are governed by similar mathematical principles. It was shown explicitly in Drăgulescu and Yakovenko (2000), Slanina (2004), and Cordier et al. (2005) that the models of pairwise money transfer can be described in a certain limit by the Fokker-Planck equation.

On the other hand, for the upper tail of the income distribution, it is reasonable to expect that $\Delta r \propto r$, that is, income changes are proportional to income itself. This is known as the proportionality principle of Gibrat (1931), and the process is called multiplicative diffusion (Silva and Yakovenko 2005). In this case, $A = ar$ and $B = br^2$, and (23) gives the power-law distribution $P(r) \propto 1/r^{\alpha+1}$, with $\alpha = 1 + a/b$.

Generally, lower-class income comes from wages and salaries, where the additive process is appropriate, whereas upper-class income comes from bonuses, investments, and capital gains, calculated in percentages, where the multiplicative process applies (Milaković 2005). However, the additive and multiplicative processes may coexist. An employee may receive a cost-of-living rise calculated in percentages (the multiplicative process) and a merit rise calculated in dollars (the additive process). In this case, we have $A = A_0 + ar$ and $B = B_0 + br^2 = b(r_0^2 + r^2)$, where $r_0^2 = B_0/b$. Substituting these expressions into (23), we find

$$P(r) = c \frac{e^{-\left(\frac{r_0}{T_r}\right) \arctan\left(\frac{r}{r_0}\right)}}{\left[1 + \left(\frac{r}{r_0}\right)^2\right]^{\frac{1+a}{2b}}}. \quad (24)$$

The distribution (24) interpolates between the exponential law for low r and the power law for high r , because either the additive or the multiplicative process dominates in the corresponding limit. The crossover between the two regimes takes place at $r \sim r_0$, where the additive and multiplicative contributions to B are equal. The distribution (24) has three parameters: the “income temperature” $T_r = A_0/B_0$, the Pareto exponent $\alpha = 1 + a/b$, and the crossover income r_0 . It is a minimal model that captures the salient features of the empirical income distribution shown in Fig. 6. A mathematically similar, but more economically oriented model was proposed in Souma and Nirei (2005) and Nirei and Souma (2007), where labor income and asset accumulation are described by the additive and multiplicative processes correspondingly. A general stochastic process with additive and multiplicative noise was studied numerically in Takayasu et al. (1997), but the stationary distribution was not derived analytically. A similar process with discrete time increments was studied by Kesten (1973). Recently, a formula similar to (24) was obtained in Fiaschi and Marsili (2007).

To verify the multiplicative and additive hypotheses empirically, it is necessary to have data on income mobility, that is, the income changes Δr of the same people from one year to another. The distribution of income changes $P(\Delta r | r)$ conditional on income r is generally not available publicly, although it can be reconstructed by researchers at the tax agencies. Nevertheless, the multiplicative hypothesis for the upper class was quantitatively verified in Fujiwara et al. (2003) and Aoyama et al. (2003) for Japan, where tax identification data is published for the top taxpayers.

The power-law distribution is meaningful only when it is limited to high enough incomes $r > r_0$. If all incomes r from 0 to ∞ follow a purely multiplicative process, then one can change to a logarithmic variable $x = \ln(r/r_*)$

in (22) and show that it gives a Gaussian time-dependent distribution $P_t(x) \propto \exp(-x^2/2\sigma^2 t)$ for x , that is, the log-normal distribution for r , also known as the Gibrat distribution (Gibrat 1931). However, the width of this distribution increases linearly in time, so the distribution is not stationary. This was pointed out by Kalecki (1945) a long time ago, but the log-normal distribution is still widely used for fitting income distribution, despite this fundamental logical flaw in its justification. In a classic paper, Champenowne (1953) showed that a multiplicative process gives a stationary power-law distribution when a boundary condition is imposed at $r_0 \neq 0$. Later, this result was rediscovered by econophysicists (Levy and Solomon 1996; Sornette and Cont 1997). In our (24), the exponential distribution of the lower class effectively provides such a boundary condition for the power law of the upper class. Notice also that (24) reduces to (18) in the limit $r_0 \rightarrow 0$, which corresponds to purely multiplicative noise $B = br^2$.

There are alternative approaches to income distribution in the economics literature. One of them, proposed by Lydall (1959), involves social hierarchy. Groups of people have leaders, who have leaders of a higher order, and so on. The number of people decreases geometrically (exponentially) with the increase of the hierarchical level. If individual income increases by a certain factor (i.e., multiplicatively) when moving to the next hierarchical level, then income distribution follows a power law (Lydall 1959). However, the original argument of Lydall can be easily modified to produce an exponential distribution. If individual income increases by a certain amount, that is, income increases linearly with the hierarchical level, then income distribution is exponential. The latter process seems to be more realistic for moderate incomes below \$ 100,000. A similar scenario is the Bernoulli trials (Feller 1966), where individuals have a constant probability of increasing their income by a fixed amount. We see that the deterministic hierarchical models and the stochastic models of additive and multiplicative income mobility represent essentially the same ideas.

Other Applications of Statistical Physics

Statistical physics was applied to a number of other subjects in economics. Because of lack of space, only two such topics are briefly discussed in this section.

Economic Temperatures in Different Countries

As discussed in section “[Empirical Data on Money and Wealth Distributions](#)” and “[Empirical Data on Income Distribution](#),” the distributions of money, wealth, and income are often described by exponential functions for the majority of the population. These exponential distributions are characterized by the parameters T_m , T_w , and T_r , which are mathematically analogous to temperature in the Boltzmann-Gibbs distribution (1). The values of these parameters, extracted from the fits of the empirical data, are generally different for different countries, i.e., different countries have different economic “temperatures.” For example, Drăgulescu and Yakovenko (2001a) found that the US income temperature was 1.9 times higher than the UK income temperature in 1998 (using the exchange rate of dollars to pounds at that time). Also, there was $\pm 25\%$ variation between income temperatures of different states within the USA (Drăgulescu and Yakovenko 2001a).

In physics, a difference of temperatures allows one to set up a thermal machine. It was argued in Drăgulescu and Yakovenko (2000) that the difference of money or income temperatures between different countries allows one to extract profit in international trade. Indeed, as discussed at the end of section “[Empirical Data on Money and Wealth Distributions](#),” the prices of goods should be commensurate with money or income temperature, because otherwise people cannot afford to buy those goods. So, an international trading company can buy goods at a low price T_1 in a “low-temperature” country and sell them at a high price T_2 in a “high-temperature” country. The difference of prices $T_2 - T_1$ would be the profit of the trading company. In this process, money (the analog of energy) flows from the “high-temperature” to the “low-temperature” country, in agreement with the second law of

thermodynamics, whereas products flow in the opposite direction. This process very much resembles what is going on in the global economy now. In this framework, the perpetual trade deficit of the USA is the consequence of the second law of thermodynamics and the difference of temperatures between the USA and “low-temperature” countries, such as China. Similar ideas were developed in more detail in Mimkes and Aruka (2005) and Mimkes (2006a), including a formal Carnot cycle for international trade.

The statistical physics approach demonstrates that profit originates from statistical non-equilibrium (the difference of temperatures), which exists in the global economy. However, it does not answer the question what is the origin of this difference. By analogy with physics, one would expect that the money flow should reduce the temperature difference and, eventually, lead to equilibration of temperatures. In physics, this situation is known as the “thermal death of the universe.” In a completely equilibrated global economy, it would be impossible to make profit by exploiting differences of economic temperatures between different countries. Although globalization of the modern economy does show a tendency toward equilibration of living standards in different countries, this process is far from straightforward, and there are many examples contrary to equilibration. This interesting and timely subject certainly requires further study.

Society as a Binary Alloy

In 1971, Thomas Schelling (Schelling 1971) proposed the now-famous mathematical model of segregation. He considered a lattice, where the sites can be occupied by agents of two types, for example, blacks and whites in the problem of racial segregation. He showed that if the agents have some probabilistic preference for the neighbors of the same type, the system spontaneously segregates into black and white neighborhoods. This mathematical model is similar to the so-called Ising model, which is a popular model for studying phase transitions in physics. In this model, each lattice site is occupied by a magnetic atom, whose magnetic moment has only two possible orientations, up or down. The interaction

energy between two neighboring atoms depends on whether their magnetic moments point in the same or in the opposite directions. In physics language, the segregation found by Schelling represents a phase transition in this system.

Another similar model is the binary alloy, a mixture of two elements which attract or repel each other. It was noticed in Mimkes (1995) that the behavior of actual binary alloys is strikingly similar to social segregation. In the following papers (Mimkes 2000, 2006b), this mathematical analogy was developed further and compared with social data. Interesting concepts, such as the coexistence curve between two phases and the solubility limit, were discussed in this work. The latter concept means that a small amount of one substance dissolves in another up to some limit, but phase separation (segregation) develops for higher concentrations. Recently, similar ideas were rediscovered in Jego and Roehner (2007), Stauffer and Schulze (2007), and Dall’Asta et al. (2007). The vast experience of physicists in dealing with phase transitions and alloys may be helpful for practical applications of such models (Lim et al. 2007).

Future Directions, Criticism, and Conclusions

The statistical models described in this review are quite simple. It is commonly accepted in physics that theoretical models are not intended to be photographic copies of reality, but rather to be caricatures, capturing the most essential features of a phenomenon with a minimal number of details. With only few rules and parameters, the models discussed in section “[Statistical Mechanics of Money Distribution](#),” “[Statistical Mechanics of Wealth Distribution](#),” and “[Data and Models for Income Distribution](#)” reproduce spontaneous development of stable inequality, which is present in virtually all societies. It is amazing that the calculated Gini coefficients, $G = 1/2$ for individuals and $G = 3/8$ for families, are actually very close to the US income data, as shown in Figs. 8 and 11. These simple models establish a baseline and a reference point for development of more

sophisticated and more realistic models. Some of these future directions are outlined below.

Future Directions

Agents with a Finite Lifespan

The models discussed in this review consider immortal agents who live forever, like atoms. However, humans have a finite lifespan. They enter the economy as young people and exit at an old age. Evolution of income and wealth as functions of age is studied in economics using the so-called overlapping-generations model. The absence of the age variable was one of the criticisms of econophysics by the economist Paul Anglin (Anglin 2005). However, the drawback of the standard overlapping-generations model is that there is no variation of income and wealth between agents of the same age, because it is a representative-agent model. It would be best to combine stochastic models with the age variable. Also, to take into account inflation of average income, (22) should be rewritten for relative income, in the spirit of (17). These modifications would allow one to study the effects of demographic waves, such as baby boomers, on the distributions of income and wealth.

Agent-Based Simulations of the Two-Class Society

The empirical data presented in section “[Empirical Data on Income Distribution](#)” show quite convincingly that the US population consists of two very distinct classes characterized by different distribution functions. However, the theoretical models discussed in section “[Statistical Mechanics of Money Distribution](#)” and “[Statistical Mechanics of Wealth Distribution](#)” do not produce two classes, although they do produce broad distributions. Generally, not much attention has been paid in the agent-based literature to simulation of two classes. One exception is Wright (2005), in which spontaneous development of employers and employees classes from initially equal agents was simulated (Wright 2007). More work in this direction would be certainly desirable.

Access to Detailed Empirical Data

A great amount of statistical information is publicly available on the Internet, but not for all types of data. As discussed in section “[Empirical Data on Money and Wealth Distributions](#),” it would be very interesting to obtain data on the distribution of balances on bank accounts, which would give information about the distribution of money (as opposed to wealth). As discussed in section “[Theoretical Models of Income Distribution](#),” it would be useful to obtain detailed data on income mobility, to verify the additive and multiplicative hypotheses for income dynamics. Income distribution is often reported as a mix of data on individual income and family income, when the counting unit is a tax return (joint or single) or a household. To have a meaningful comparison with theoretical models, it is desirable to obtain clean data where the counting unit is an individual. Direct collaboration with statistical agencies would be very useful.

Economies in Transition

Inequality in developed capitalist countries is generally quite stable. The situation is very different for former socialist countries making a transition to a market economy. According to the World Bank data (Drăgulescu and Yakovenko 2003), the average Gini coefficient for family income in eastern Europe and the former Soviet Union jumped from 25% in 1988 to 47% in 1993. The Gini coefficient in the socialist countries before the transition was well below the equilibrium value of 37.5% for market economies. However, the fast collapse of socialism left these countries out of market equilibrium and generated a much higher inequality. One may expect that, with time, their inequality will decrease to the equilibrium value of 37.5%. It would be very interesting to trace how fast this relaxation takes place. Such a study would also verify whether the equilibrium level of inequality is universal for all market economies.

Relation to Physical Energy

The analogy between energy and money discussed in section “[Conservation of Money](#)” is a formal mathematical analogy. However, actual

physical energy with low entropy (typically in the form of fossil fuel) also plays a very important role in the modern economy, as the basis of current human technology. In view of the looming energy and climate crisis, it is imperative to find realistic ways for making a transition from the current “disposable” economy based on “cheap” and “unlimited” energy and natural resources to a sustainable one. Heterogeneity of human society is one of the important factors affecting such a transition. Econophysics, at the intersection of energy, entropy, economy, and statistical physics, may play a useful role in this quest (Defilla 2007).

Criticism from Economists

As econophysics is gaining popularity, some criticism has appeared from economists (Anglin 2005), including those who are closely involved with the econophysics movement (Lux 2005; 2008; Gallegati et al. 2006). This reflects a long-standing tradition in economic and social sciences of writing critiques on different schools of thought. Much of the criticism is useful and constructive and is already being accommodated in econophysics work. However, some criticism results from misunderstanding or miscommunication between the two fields and some from significant differences in scientific philosophy. Several insightful responses to the criticism have been published (McCauley 2006; Richmond et al. 2006c; Rosser 2006a); see also (Stauffer 2004; Rosser 2006b). In this section, we briefly address the issues that are directly related to the material discussed in this review.

Awareness of Previous Economics Literature

One complaint of Anglin (2005), Lux (2005), (2008), and Gallegati et al. (2006) is that physicists are not well aware of the previous economics literature and either rediscover known results or ignore well-established approaches. To address this issue, it is useful to keep in mind that science itself is a complex system, and scientific progress is an evolutionary process with natural selection. The sea of scientific literature is enormous, and nobody knows it all. Recurrent rediscovery of

regularities in the natural and social world only confirms their validity. Independent rediscovery usually brings a different perspective, broader applicability range, higher accuracy, and better mathematical treatment, so there is progress even when some overlap with previous results exists. Physicists are grateful to economists for bringing relevant and specific references to their attention. Since the beginning of modern econophysics, many old references have been uncovered and are now routinely cited.

However, not all old references are relevant to the new development. For example, Gallegati et al. (2006) complained that the econophysics literature on income distribution ignores the so-called Kuznets hypothesis (Kuznets 1955). The Kuznets hypothesis postulates that income inequality first rises during an industrial revolution and then decreases, producing an inverted-U-shaped curve. Gallegati et al. (2006) admitted that, to date, the large amount of literature on the Kuznets hypothesis is inconclusive. Kuznets (1955) mentioned that this hypothesis applies to the period from colonial times to the 1970s; however, the empirical data for this period are sparse and not very reliable. The econophysics literature deals with reliable volumes of data for the second half of the twentieth century, collected with the introduction of computers. It is not clear what is the definition of industrial revolution and when exactly it starts and ends. The chain of technological progress seems to be continuous (steam engine, internal combustion engine, cars, plastics, computers, Internet), so it is not clear where the purported U-curve is supposed to be placed in time. Thus, the Kuznets hypothesis appears to be, in principle, unverifiable and unfalsifiable. The original paper by Kuznets (1955) actually does not contain any curves, but it has one table filled with made-up, imaginary data! Kuznets admits that he has “neither the necessary data nor a reasonably complete theoretical model” (p. 12 in Kuznets (1955)). So, this paper is understandably ignored by the econophysics community. In fact, the data analysis for 1947–1984 shows amazing stability of income distribution (Levy 1987), consistent with Fig. 11. The increase of inequality in the 1990s resulted from growth of

the upper class relative to the lower class, but the relative inequality within the lower class remains very stable, as shown in Fig. 7.

Reliance on Visual Data Analysis

Another complaint of Gallegati et al. (2006) is that econophysicists favor graphic analysis of data over the formal and “rigorous” testing prescribed by mathematical statistics, as favored by economists. This complaint goes against the trend of all sciences to use increasingly sophisticated data visualization for uncovering regularities in complex systems. The thick IRS publication 1304 (Internal Revenue Service 1999) is filled with data tables, but has virtually no graphs. Despite the abundance of data, it gives a reader no idea about income distribution, whereas plotting the data immediately gives insight. However, intelligent plotting is the art with many tools, which not many researchers have mastered. The author completely agrees with Gallegati et al. (2006) that too many papers mindlessly plot any kind of data on a log-log scale, pick a finite interval, where any smooth curved line can be approximated by a straight line, and claim that there is a power law. In many cases, replotting the same data on a log-linear scale converts a curved line into a straight line, which means that the law is actually exponential.

Good visualization is extremely helpful in identifying trends in complex data, which can then be fitted to a mathematical function; however, for a complex system, such a fit should not be expected with infinite precision. The fundamental laws of physics, such as Newton’s law of gravity or Maxwell’s equations, are valid with enormous precision. However, the laws in condensed matter physics, uncovered by experimentalists with a combination of visual analysis and fitting, usually have much lower precision, at best 10% or so. Most of these laws would fail the formal criteria of mathematical statistics. Nevertheless these approximate laws are enormously useful in practice, and everyday devices engineered on the basis of these laws work very well for all of us.

Because of the finite accuracy, different functions may produce equally good fits.

Discrimination between the exponential, Gamma, and log-normal functions may not be always possible (Banerjee et al. 2006). However, the exponential function has fewer fitting parameters, so it is preferable on the basis of simplicity. The other two functions can simply mimic the exponential function with a particular choice of the additional parameters (Banerjee et al. 2006). Unfortunately, many papers in mathematical statistics introduce too many fitting parameters into complicated functions, such as the generalized beta distribution mentioned in Gallegati et al. (2006). Such overparameterization is more misleading than insightful for data fitting.

Quest for Universality

Gallegati et al. (2006) criticized physicists for trying to find universality in economics data. They also seemed to equate the concepts of power law, scaling, and universality. These are three different, albeit overlapping, concepts. Power laws usually apply only to a small fraction of data at the high ends of various distributions. Moreover, the exponents of these power laws are usually nonuniversal and vary from case to case. Scaling means that the shape of a function remains the same when its scale changes. However, the scaling function does not have to be a power-law function. A good example of scaling is shown in Fig. 7, where income distributions for the lower class collapse on the same exponential line for about 20 years of data. We observe amazing universality of income distribution, unrelated to a power law. In a general sense, the diffusion equation is universal, because it describes a wide range of systems, from dissolution of sugar in water to a random walk in the stock market.

Universalities are not easy to uncover, but they form the backbone of regularities in the world around us. This is why physicists are so interested in them. Universalities establish the first-order effect, and deviations represent the second-order effect. Different countries may have somewhat different distributions, and economists often tend to focus on these differences. However, this focus on details misses the big picture that, in the first approximation, the distributions are quite similar and universal.

Theoretical Modeling of Money, Wealth, and Income

It was pointed out in Anglin (2005), Gallegati et al. (2006), and Lux (2008) that many econophysics papers confuse or misuse the terms for money, wealth, and income. It is true that terminology is sloppy in many papers and should be refined. However, the terms in Drăgulescu and Yakovenko (2000) and Chakraborti and Chakrabarti (2000) are quite precise, and this review clearly distinguishes between these concepts in section “[Statistical Mechanics of Money Distribution](#),” “[Statistical Mechanics of Wealth Distribution](#),” and “[Data and Models for Income Distribution](#).”

One contentious issue is about conservation of money. Gallegati et al. (2006) agree that “transactions are a key economic process, and they are necessarily conservative,” that is, money is indeed conserved in transactions between agents. However, Anglin (2005), Gallegati et al. (2006), and Lux (2008) complain that the models of conservative exchange do not consider production of goods, which is the core economic process and the source of economic growth. Material production is indeed the ultimate goal of an economy, but it does not violate conservation of money by itself. One can grow coffee beans, but nobody can grow money on a money tree. Money is an artificial economic device that is designed to be conserved. As explained in section “[Statistical Mechanics of Money Distribution](#),” the money transfer models implicitly assume that money in transactions is voluntarily paid for goods and services generated by production for the mutual benefit of the parties. In principle, one can introduce a billion variables to keep track of every coffee bean and other product of the economy. What difference would it make for the distribution of *money*? Despite the claims in Anglin (2005) and Gallegati et al. (2006), there is no contradiction between models of conservative exchange and the classic work of Adam Smith and David Ricardo. The difference is only in the focus: We keep track of money, whereas they keep track of coffee beans, from production to consumption. These approaches address different questions, but do not contradict each other. Because money constantly circulates in the system as payment for production and

consumption, the resulting statistical distribution of money may very well not depend on what exactly is produced and in what quantities.

In principle, the models with random transfers of money should be considered as a reference point for developing more sophisticated models. Despite the totally random rules and “zero intelligence” of the agents, these models develop well-characterized, stable, and stationary distributions of money. One can modify the rules to make the agents more intelligent and realistic and see how much the resulting distribution changes relative to the reference one. Such an attempt was made in Lux (2005) by modifying the model of Silver et al. (2002) with various more realistic economic ingredients. However, despite the modifications, the resulting distributions were essentially the same as in the original model. This example illustrates the typical robustness and universality of statistical models: Modifying details of microscopic rules does not necessarily change the statistical outcome.

Another misconception, elaborated in Lux (2005), (2008), is that the money transfer models discussed in section “[Statistical Mechanics of Money Distribution](#)” imply that money is transferred by fraud, theft, and violence, rather than voluntarily. One should keep in mind that the catchy labels “theft-and-fraud,” “marriage-and-divorce,” and “yard-sale” were given to the money transfer models by the journalist Brian Hayes (2002) in a popular article. Econophysicists who originally introduced and studied these models do not subscribe to this terminology, although the early work of Angle (1986) did mention violence as one source of redistribution. In the opinion of the author, it is indeed difficult to justify the proportionality rule (8), which implies that agents with high balances pay proportionally greater amounts in transactions than agents with low balances. However, the additive model of Drăgulescu and Yakovenko (2000), where money transfers Δm are independent of money balances m_i of the agents, does not have this problem. As explained in section “[The Boltzmann-Gibbs Distribution of Money](#),” this model simply means that all agents pay the same prices for the same product, although prices may be different for different

products. So, this model is consistent with voluntary transactions in a free market.

McCauley (2006) argued that conservation of money is violated by credit. As explained in section “[Models with Debt](#),” credit does not violate conservation law, but creates positive and negative money without changing net worth. Negative money (debt) is as real as positive money. McCauley (2006) claimed that money can be easily created with the tap of a computer key via credit. Then why would an employer not tap the key and double salaries, or a funding agency double research grants? Because budget constraints are real. Credit may provide a temporary relief, but sooner or later it has to be paid back. Allowing debt may produce a double-exponential distribution as shown in Fig. 3, but it does not change the distribution fundamentally.

As discussed in section “[Conservation of Money](#),” a central bank or a central government can inject new money into the economy. As discussed in section “[Statistical Mechanics of Wealth Distribution](#),” wealth is generally not conserved. As discussed in section “[Data and Models for Income Distribution](#),” income is different from money and is described by a different model (22). However, the empirical distribution of income shown in Fig. 6 is qualitatively similar to the distribution of wealth shown in Fig. 5, and we do not have data on money distribution.

Conclusions

The “invasion” of physicists into economics and finance at the turn of the millennium is a fascinating phenomenon. The physicist Joseph McCauley proclaims that “Econophysics will displace economics in both the universities and boardrooms, simply because what is taught in economics classes doesn’t work” (Ball 2006; McCauley 2004; Farmer et al. 2005; Samanidou et al. 2007; Econophysics forum 2008). Although there is some truth in his arguments (McCauley 2006), one may consider a less radical scenario. Econophysics may become a branch of economics, in the same way as games theory, psychological economics, and now

agent-based modeling became branches of economics. These branches have their own interests, methods, philosophy, and journals. The main contribution from the infusion of new ideas from a different field is not in answering old questions, but in raising new questions. Much of the misunderstanding between economists and physicists happens not because they are getting different answers, but because they are answering different questions.

The subject of income and wealth distributions and social inequality was very popular at the turn of another century and is associated with the names of Pareto, Lorenz, Gini, Gibrat, and Champernowne, among others. Following the work by Pareto, attention of researchers was primarily focused on the power laws. However, when physicists took a fresh, unbiased look at the empirical data, they found a different, exponential law for the lower part of the distribution. The motivation for looking at the exponential law, of course, came from the Boltzmann-Gibbs distribution in physics. Further studies provided a more detailed picture of the two-class distribution in a society. Although social classes have been known in political economy since Karl Marx, the realization that they are described by simple mathematical distributions is quite new. Demonstration of the ubiquitous nature of the exponential distribution for money, wealth, and income is one of the new contributions produced by econophysics.

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